

NUCLEAR MAGNETIC RESONANCE OF
PARAMAGNETIC SOLUTIONS

by

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SUMMARY

The weak complexes formed in aqueous solution between cobalt (II) and alcohols, polyols and carbohydrates have been studied by Nuclear Magnetic Resonance (N.M.R.) spectroscopy and the contact shifts obtained have been found to depend both on the stability and the stereochemistry of the complex: while negative contact shifts have been found to be predominant, in some cases positive pseudocontact shifts also appear to be of importance. The contact shifts obtained are governed by the fraction of ligand complexed and the shifts in the complex and the line widths by these two factors and also the transverse relaxation processes within the complex.

It has been possible to distinguish between isomeric α -diols by this method and to analyse a mixture of such diols, and it has been shown that the method could be used to study the products of a reaction which involves the formation of an α -diol.

The effect of copper (II) on the N.M.R. spectra of sulphur compounds has also been studied and it has been shown that the selective line broadening observed for protons α - to a sulphur atom is scalar in origin and governed by the fraction of ligand complexed and the transverse relaxation time in the complex. It has been found that the extent of line broadening is dependent on the copper salt used. The method may be used to distinguish between sulphur atoms in different environments and also to identify the N.M.R. signals arising from protons on carbon atoms

adjacent to a sulphur atom in a sulphide.

Preliminary studies on other systems are also reported and it has been shown that copper (II) also produces marked selective line broadening in azine compounds where complex formation occurs at the nitrogen atom.

INTRODUCTION

Complexing with paramagnetic ions or other paramagnetic species can have profound effects on the Nuclear Magnetic Resonance (N.M.R.) spectra of ligands, changes being produced by the unpaired electron(s) in the paramagnetic species. In general, three aspects of such effects may be distinguished;

- a) Shifts in the resonance positions of the ligand N.M.R. signals,
- b) Broadening of the signals, and
- c) Changes in the multiplicity of signals from a nucleus close to a complexing site which is coupled to other nuclei, and of those of the nuclei to which it is coupled.

Such effects are of considerable interest, both intrinsically and in view of their potential application to other fields, and their exploitation as an aid in structure determination appears a promising field.

While an increasing volume of work has been done on the N.M.R. spectra of paramagnetic solutions, especially in recent years, most of the work hitherto done has been from the viewpoint of physical and inorganic chemists, seeking to understand the physical processes at work and the type of bonding occurring in the complexes. As yet no serious and systematic investigation has been reported of situations which are of significance to organic chemists, and no attempt has been made to use such effects as a tool in the elucidation of the structure of compounds.

Potential applications of the effects produced by complexing with paramagnetic ions are many, as shown by the examples listed

below.

1. Information derived from shifts in resonance positions.

a. Elucidation of the presence and environment of certain functional groups which act as complexing and donor sites, e.g. in carboxylic acids, alcohols and polyols, hydroxy acids, amines, amino acids, etc.

b. Simplification of spectra by transformation of e.g. AB systems to AX systems through the effects of selective contact shifts.

c. Information about the molecular geometry of complexes through the interpretation of pseudocontact shifts.

d. Information about hyperfine interactions in the complex, and thus about the mechanism of transfer of unpaired electron spin in molecules.

2. Information derived from line broadening

a. Recognition of functional groups and their environment.

b. Simplification of spectra by spin-decoupling through the medium of paramagnetic relaxation.

c. Information about relaxation mechanisms and exchange rates.

With the aim of extending such studies in the field of organic chemistry, specifically with regard to their use as aids in structure determination, complexes of alcohols and polyols with cobalt (II), and of sulphur containing compounds with Cu (II) have been studied by N.M.R., and the results of these studies are reported later in this thesis. The results obtained from

preliminary studies of other similar systems are also reported.

However, as an understanding of the manner in which complexing with a paramagnetic species affects the N.M.R. spectrum of a ligand is essential to the interpretation of the results of these studies, there first follows a review of the effects of paramagnetic ions on the N.M.R. spectra of ligands in solution.

PART 2: EFFECT OF PARAMAGNETIC IONS ON LIGAND N.M.R. SIGNALS

(I) Introduction

As noted earlier, complexing with paramagnetic species can affect the ligand N.M.R. signals in two main ways. On the one hand the signals may be shifted, often by a very large amount, and secondly the signals may be broadened due to the effect of the unpaired electron on the relaxation times of the nuclei. Both of these effects are due to interaction between the unpaired electron(s) and nuclear spins; such interactions being much more dramatic than the analogous more familiar interactions between nuclei since the magnetic moment of an unpaired electron is about 10^3 times that of atomic nuclei.

In this review the mechanisms responsible for the shift and relaxation effects will be considered in turn. Both effects are profoundly modified by chemical exchange of the ligand between the paramagnetic environment in the complex and the diamagnetic one of the bulk solution; such exchange effects will be considered later in a separate section. Finally, various systems in which these effects have been observed will be discussed.

(II) Contact Shifts

In paramagnetic species, interaction of nuclear spins with the unpaired electron spin can produce chemical shifts which are many times larger than the ordinary shifts obtained in diamagnetic molecules, and which show characteristic temperature dependence. Such interactions are shown in Electron Spin Resonance (E.S.R.)

spectroscopy as hyperfine structure.

These large shifts produced by the electron spin in N.M.R. spectra are due to the very strong local magnetic fields resulting from the hyperfine interaction, and might be expected, at least at first sight, to lead to a doublet of separation equal to the E.S.R. hyperfine coupling constant A , where A is measured in Mc/s and not c/s. However this is generally not observed in practice, especially if the electronic relaxation time is long, as the lines would be extremely broad, although the E.S.R. lines may be fairly sharp.

However, if the electronic relaxation time is short, then the nuclei see only a time averaged local field proportional to the mean value of the electron spin component which is thus much smaller. If $1/T_c \gg A$ or $1/T_{1e} \gg A$, where $1/T_{1e}$ is the electronic spin-lattice relaxation time and $1/T_c$ the rate of chemical exchange, then electronic relaxation times are so short, or exchange interactions are sufficiently effective that the E.S.R. lines are too broad for resolution. Either or both of these conditions however render the N.M.R. spectrum observable¹, the lines often being quite narrow. In this case the isotropic contact doublet structure is not obtained, only a singlet line being recorded. Where this averaging occurs, due to the Boltzman distribution of populations the two electronic spin states are not equally populated, and so the signal recorded is a weighted mean of the isotropically shifted lines, and hence there is a shift from the diamagnetic resonance position.

The first expression for this contact shift, due to Bloembergen^{2a}, in its most general form is given by,

$$\frac{\Delta H}{H} = \frac{\Delta \omega}{\omega} = \frac{\Delta \nu}{\nu} = - \frac{4}{9} \frac{A \gamma_e}{\gamma_I} \frac{g \beta S(S+1)I(I+1)}{kT} \quad (1)$$

where H, ω, ν define the units of the resonance frequency; A is the hyperfine interaction constant; γ_e, γ_I the electronic and nuclear gyromagnetic ratios respectively; g the electronic g factor; β the Bohr magneton; I, S the nuclear and electronic spin quantum numbers respectively; k the Boltzman constant and T the absolute temperature.

For protons, where $I = 1/2$, $4I(I+1)/9kT$ reduces to $1/3kT$.

Various expressions have appeared in the literature where the denominator includes the terms $6kT^{3,4}$, $6S kT^5$ and $6S' kT^6$, the most general form of the Bloembergen expression thus being⁶ for the multi-unpaired electron case

$$\frac{\Delta \nu}{\nu} = \frac{-Ag \beta S(S+1) \gamma_e}{6S' kT \gamma_I} \quad (2)$$

where, in this case S is the total unpaired electron spin, and S' the unpaired electron spin available for delocalisation. Thus this more general expression takes account of such cases, which occur with some transition ions, where although all the unpaired electrons contribute to the effective magnetic moment, only part of the unpaired electron spin can be delocalised through the metal-ligand bonds in a complex, e.g. octahedral $Co(II)$ complexes³.

Where the ground state of the complexed species is diamagnetic, but there exists a higher, excited paramagnetic state

which is thermally accessible, such that a diamagnetic \rightleftharpoons paramagnetic equilibrium may be set up, the contact shift expression then includes a free energy term. Here too, various expressions have appeared in the literature.

McConnell and Chestnut¹ first introduced the expression

$$\frac{\Delta\nu}{\nu} = - \frac{2A \gamma_e}{\gamma_H} \frac{g\beta}{kT} [\exp. (\Delta G/kT) + 3]^{-1} \quad (3)$$

where ΔG is the free energy difference between the two states which was used by Phillips and Benson⁷. Eaton *et al.*⁸ modified this expression by multiplying by a factor of $(S + 1)/4$, or when $S = 1$, by a factor of $1/2S$. Their expression has been used by many workers, Holm⁹ pointing out that the introduction of the $2S$ term implies a definition of spin density such that the sum of the individual spin densities is $2S$ and not unity as was the original definition¹. However, the expression has been further modified by Horrocks¹⁰ who pointed out that in the previous derivations electron degeneracy was improperly taken into account, his general expression being

$$\frac{\Delta\nu}{\nu} = \frac{-A \gamma_e}{\gamma_H} \frac{g\beta S(S + 1)}{6SkT} [\exp. (\Delta G /kT) + 1]^{-1} \quad (4)$$

which now seems to be generally accepted.^{11,12}

In a paramagnetic complex species the magnitude of the recorded N.M.R. contact shift depends on the value of the coupling constant A and its sign, both of which can be obtained from equation (2). The value of A depends on the unpaired spin density, and so, in a ligand giving different N.M.R. signals the value of

the coupling constant is a measure of the unpaired spin density at that position, and so of the effectiveness of delocalisation of unpaired spin density to that position.

Delocalisation of unpaired spin density can occur through the σ -bond system of the ligand, or through a π -bond system, or both. If delocalisation is through a σ -bond system then the signs of the various coupling constants, and so of the contact shifts obtained are all the same, and this, and the fact that delocalisation is rapidly attenuated along a σ -bond system enables this type of delocalisation mechanism to be easily recognised.

However, if delocalisation occurs through a π -bond system then an alternation in signs of contact shift at successive positions along a chain or ring system is obtained, this being characteristic of a π -mechanism. Thus, considering a π -bond system, e.g. an aromatic ring system as in pyridine, if electron transfer from a paramagnetic ion reaches say the α - carbon via the co-ordinating nitrogen in the π -system, this unpaired spin reaches a proton 1s orbital via a π - σ polarisation mechanism in which the sign of the unpaired spin induced in the hydrogen 1s orbital is of opposite sign to that on the carbon atom to which it is attached. Similarly the sign of the unpaired spin reaching the β -carbon atom is of opposite sign to that on the α -carbon, such alternation in sign occurring all along the π -system. Another typical sign of a π -delocalisation mechanism is that substitution of a proton by a methyl group results in a methyl contact shift opposite in sign to that of the proton replaced.

The relationship between unpaired spin density and the isotropic hyperfine coupling constant for a $\dot{\text{C}}\text{-H}$ fragment was derived by McConnell and Chestnut¹ as

$$A = Q\rho \quad \text{---} \quad (5)$$

where ρ is the unpaired spin density centred on the carbon orbital, and Q is an empirical constant and has a value of about -22.5 gauss or -63 Mc/s. Thus substitution of the coupling constants derived from contact shift values using equation 2 into equation 5 enables a spin density map of a π -system chelated to a paramagnetic ion to be drawn.

For a $\dot{\text{C}}\text{-CH}_3$ fragment however no such relationship exists, each case being different as unpaired spin density reaches the methyl protons by a direct hyperconjugative mechanism and not a π - σ polarisation mechanism.

The McConnell and Chestnut equation has also been generalised from the single electron to the many electron case by inclusion of a $2S$ factor¹³, to give

$$A = \frac{Q\rho}{2S} \quad \text{---} \quad (6)$$

(III) Pseudocontact shifts

Isotropic nuclear resonance shifts can also arise through anisotropy in the electronic g tensors. These arise from the combined effects of electron spin-orbit interaction, (electron orbit)-(nuclear spin) dipolar coupling, and (electron spin)-(nuclear spin) dipolar coupling, and are called pseudocontact shifts.

McConnell and Robertson¹⁴, for a complex of axial symmetry developed equations giving the pseudocontact shift both in a polycrystalline solid and in solution, the difference between the two providing in principle a method of distinguishing between Fermi contact and pseudocontact shifts since they differ by a factor dependent only on the differences in the electronic g tensors, which can easily be measured.

In solution, where tumbling of the complex occurs, the expression for the pseudocontact shifts depend on the relative magnitude of the tumbling time. McConnell and Robertson concluded that in practice the most probable case would be that where the value of the tumbling correlation time τ_c was such that $1/\tau_c \gg |g_{\parallel} - g_{\perp}| H_0 \hbar$ and, where $T_{1e} \gg \tau_c$, they thus derived the expression for the pseudocontact shift for axial symmetry as

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{soln.}} = \frac{|B|^2 S(S+1)}{27r^3KT} [(g_{\parallel} + 2g_{\perp})(g_{\parallel} - g_{\perp})] (3\cos^2\chi - 1) \quad (7)$$

where H_0 is the applied magnetic field, $\hbar = h/2\pi$, where h is Planks constant, g_{\parallel} , g_{\perp} the electronic g tensors parallel and perpendicular to the principal symmetry axis respectively; r the distance between the paramagnetic centre and the nuclei; and χ the angle between the distance vector and the principal symmetry axis.

Using the same inequality conditions as above, LaMar et al.¹⁵ extended this expression to complexes of tetrahedral symmetry.

Later however La Mar¹⁶ pointed out that the condition assumed to be most probable by McConnell and Robertson, that $T_{1e} \gg \tau_c$,

was in fact not the case for the bis-(triarylphosphine) complexes of Ni(II) and Co(II) halides, and, by implication, perhaps other similar complexes of these ions. They calculated that in fact in these complexes $\tau_c \gg T_{1e}$, and thus the alternative form derived by McConnell and Robertson was applicable, which, after correcting the misprinted signs in the original paper¹⁴, is

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{soln.}} = - \frac{|\mu|^2 S(S+1)}{45 r^3 k T} [3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2] (3\cos^2\chi - 1) \quad (8)$$

which, like the alternative form is strictly only correct for systems having no residual ground state orbital angular momentum¹⁷. The analogous expression applicable to tetrahedral complexes has also been derived¹⁶.

That the inequality condition $\tau_c \gg T_{1e}$ can in fact occur, contrary to what had previously been supposed, thus tends to cast doubt on the results of much of the earlier work on pseudocontact shifts, especially on the values of $|g_{\parallel} - g_{\perp}|$ ^{16a}. As pointed out by Eaton⁶ if in fact $\tau_c \gg T_{1e}$ then the pseudocontact shifts will be larger by a factor of $3(3g_{\parallel} + 4g_{\perp})/5(g_{\parallel} + 2g_{\perp})$ than if $T_{1e} \gg \tau_c$. Such a correction, whilst changing the absolute value of the anisotropy, will not affect any relative qualitative relationship obtained using the former expression for different protons in the same molecule since in such a case only the ratios of the geometric terms were compared.

The most studied ion which gives rise to pseudocontact shifts has been Co(II), the pseudocontact shifts being evaluated by comparison of the shifts obtained with those of the corresponding Ni(II) complex in which it was assumed that no pseudocontact

contribution is present. In this method the shift ratios for the Co(II) complex are normalised to agree with the Ni(II) shift ratios, and the difference at each position in the molecule assumed to be due to pseudocontact interaction. The ratios of the pseudocontact shifts within the molecule complexed are constant irrespective of the value of the anisotropy term since they depend only on the geometric term of the pseudocontact shift expression and hence are unaffected by the inequality conditions implied in the expression used. However the absolute values of the anisotropies calculated from pseudocontact shift data are dependent on the actual pseudocontact expression used. Hence anisotropy values calculated using the previous expression and reported in the literature may in fact be in error by the factor above if the latter pseudocontact expression does in fact hold for those particular cases.

(IV) Relaxation Times, Line Shape and Line Width

a. Relaxation Times

In N.M.R. spectroscopy two relaxation times exist which govern the line widths of the N.M.R. signals and, in suitable situations, may also determine whether or not nuclear spin-spin splitting is observed. These relaxation times are the spin-lattice relaxation time, T_1 , and the transverse relaxation time, T_2 .

The spin-lattice relaxation time T_1 depends on the degree of coupling of the nuclei to the thermal motion of the molecules in the liquid, i.e. the lattice, and is a measure of the time taken

to establish the Boltzman equilibrium between nuclei in the low and high energy spin states. If the interaction is strong, then spin-lattice relaxation is strong, and so T_1 is short, the opposite being the case if the interaction is weak.

This relaxation time gives rise to line broadening of the N.M.R. signal as it represents a finite lifetime of both energy states because of the possibility of transitions between the two states being induced by other molecular degrees of freedom, hence the name spin-lattice relaxation time. The line width of the N.M.R. signal due to T_1 can be obtained from the Uncertainty Principle written in the form $\Delta E \cdot \Delta t = \hbar$, and since $\Delta E = h\Delta\nu$, this gives the uncertainty in the frequency of absorption as $1/2\pi\Delta t$, and so the line width measured on a frequency scale will be of the order of $1/T_1$.

The transverse relaxation time, T_2 , also introduced by Bloch¹³ in his solution of the N.M.R. phenomenological equations, represents the relaxation time in the transverse direction to the z-component of the applied external magnetic field, hence the name. This relaxation time accounts for the line width when the spin-lattice relaxation time is too long to account for the observed line width, and may be associated with the rate of loss of phase of the precessing group of nuclei within the co-ordinate frame of the N.M.R. system.

In the Bloch formulation these relaxation times are expressed in terms of the time derivatives of the magnetisation in the direction of the x, y, and z axes, but the relationship between T_2 and the line width is more readily seen when T_2 is expressed in

terms of the maximum of the line shape function.

Thus, $T_2 = 1/2 \cdot g(\nu)_{\text{maxm.}}$, where

$$g(\nu) = \frac{2 T_2}{1 + 4 \pi^2 T_2^2 (\nu_0 - \nu)^2} \quad \text{--- (9)}$$

where ν = absorption frequency; ν_0 = frequency of maximum absorption.

This expression describes a Lorentzian curve whose width at half height is determined by the reciprocal of T_2 . Thus, on a frequency scale,

$$\frac{1}{T_2} = \pi \Delta \nu_{1/2} \quad \text{--- (10)}$$

where $\Delta \nu_{1/2}$ in c/s is the width at half peak height.

b. Relaxation effects in the absence of complexing

For nuclei of spin $I = 1/2$, the electric quadrupole moment is zero and hence relaxation times can be fairly large, of the order of a few seconds. Addition of paramagnetic species to such a diamagnetic solution can produce marked changes in relaxation times as the magnetic moment of an unpaired electron is about 10^3 times that of an atomic nucleus.

The only agency that can cause changes in the nuclear energy states is a magnetic field fluctuating at the nuclear magnetic resonance frequency for that value of applied external field H_0 , and in a diamagnetic liquid these fluctuating magnetic fields arise from the motion of the molecules which contain the magnetic nuclei. At any point there is a small field set up by the random distribution of the nuclei at that point, and if the nuclei are in thermal

motion then the magnetic field set up by them fluctuates with a frequency spectrum corresponding to the molecular motion. This fluctuating magnetic field can be split up into components, and only that component which is close to the N.M.R. frequency is effective in inducing spin-lattice relaxation, and the more intense that component, the shorter is T_1 .

In a liquid the frequency of molecular motion is about 10^{11} c/s, and as the normal N.M.R. frequency is about 10^7 c/s, the component of the fluctuating field which can induce spin-lattice relaxation is weak, and hence T_1 is long.

However, introduction of paramagnetic ions to a solution causes local field fluctuations to increase in intensity due to the much larger magnetic moment of the unpaired electron, thus increasing the intensity of the component affecting spin-lattice relaxation, and hence T_1 becomes shorter. Normally the transverse relaxation time T_2 is also shortened, and as this has an inverse relationship to the line width the N.M.R. signal is broadened.

If however the electron is itself 'flipping over' with a relaxation time T_e which is much shorter than the correlation time for Brownian diffusion then the local field fluctuations produced by the electron will be partially averaged out and reduced in intensity and so T_1 will be less affected and the lines may be fairly narrow in suitable cases.

The relaxation effects produced by the unpaired electron were first explained by Bloembergen, Purcell and Pound¹⁹ who attributed the relaxation effects to diffusional Brownian motion in the vicinity of the paramagnetic ion, $1/T_1$ being directly proportional

to the concentration of the paramagnetic ion and to its mean square effective magnetic moment.

c. Relaxation in the complexed species

The impetus to studies of relaxation phenomena was given by Bloch, Hansen and Packards²⁰ discovery that paramagnetic ions decreased the relaxation times of water, and studies of such systems led to a deeper understanding of relaxation effects in general.

The early diffusional Browning motion theory was followed by a dipole-dipole interaction theory, but when this failed to account for the effects produced by certain paramagnetic ions the isotropic hyperfine contact interaction theory was developed to account for these apparently anomalous effects. In these early studies the paramagnetic ions were found to fall into two groups; those which affected T_1 and T_2 equally such that $T_1/T_2 \approx 1$ ^{21, 22}, and those which gave $T_1/T_2 > 1$ ^{22, 23}. Solomon²⁴ developed expressions to account for dipole-dipole interactions which were modified by Bloembergen²⁶ to include scalar interaction terms, the resulting Bloembergen-Solomon equations being the basic expressions for relaxation effects in paramagnetic complexes. These relaxation time equations are:

$$\frac{1}{T_{1M}} = \frac{2}{15} \frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \left[3\tau_c + \frac{7\tau_c}{1+\omega_S^2\tau_c^2} \right] + \frac{2}{3} \frac{S(S+1)A^2}{\hbar^2} \left[\frac{\tau_e^{(2)}}{1+\omega_S^2\tau_e^2} \right] \quad (11)$$

$$\frac{1}{T_{2M}} = \frac{1}{15} \frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \left[7\tau_c + \frac{13\tau_c}{1+\omega_S^2\tau_c^2} \right] + \frac{1}{3} \frac{S(S+1)A^2}{\hbar^2} \left[\tau_e + \frac{\tau_e}{1+\omega_S^2\tau_e^2} \right] \quad (12)$$

the first terms on the right hand side being the dipolar term, the second the scalar terms.

The subscript M refers to the metal complex, r is the distance from the paramagnetic centre to the nucleus, γ_I is the nuclear gyromagnetic ratio, τ_c the correlation time for anisotropic dipolar interaction, τ_e the correlation time for isotropic contact interaction, ω_s the electronic Larmor precessional frequency, and the other terms are as have previously been defined.

The relationship between the correlation times is²⁵

$$\frac{1}{\tau_c} = \frac{1}{\tau_e} + \frac{1}{\tau_r} \text{ where } \frac{1}{\tau_e} = \frac{1}{\tau_s} + \frac{1}{\tau_h} \text{ and so } \frac{1}{\tau_c} = \frac{1}{\tau_s} + \frac{1}{\tau_h} + \frac{1}{\tau_r}$$

where τ_r is the correlation time for tumbling of the complex, τ_h the correlation time for chemical exchange, i.e. the co-ordination time, and τ_s the correlation time for electron spin relaxation.

Which term dominates in the expressions for T_{1M} and T_{2M} will vary from ion to ion, depending on the relative values of the correlation times.

Under conditions of slow exchange τ_e is dominated by τ_s . For ions with moderately fast electron relaxation times (especially for Co(II), Fe(II) and Ni(II)) τ_c is also dominated by τ_s . For Co(II)²⁵ $\tau_s \sim 5 \times 10^{-13}$ sec., and hence $(\omega_s \tau_c)^2 \ll 1$ and $(\omega_s \tau_e)^2 \ll 1$, and the Bloembergen-Solomon equations reduce to;

$$\frac{1}{T_{1M}} = \frac{1}{T_{2M}} = \frac{4}{3} \frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \cdot \tau_s + \frac{2}{3} \frac{S(S+1)A^2}{h^2} \cdot \tau_s \quad \text{---(13)}$$

which is also applicable in the slow exchange limit.²⁶

If however τ_s is quite long, e.g. for Mn(II) where $\tau_s \sim 1 \times 10^{-8}$ sec²⁵, then T_{2M} is dominated by the scalar term, but T_{1M}

is dominated by the dipolar term and the scalar term can be ignored in comparison with the dipolar term, and so

$$\frac{1}{T_{1M}} = \frac{2}{5} \frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \cdot \tau_c \quad \text{--- (14)}$$

$$\frac{1}{T_{2M}} = \frac{7}{15} \frac{S(S+1)g^2\beta^2\gamma_I^2}{r^6} \cdot \tau_c + \frac{1}{3} \frac{S(S+1)A^2}{\hbar^2} \cdot \tau_e \quad \text{--- (15)}$$

in which τ_c is dominated by τ_r and τ_e by τ_s , except under conditions of rapid exchange such that $\tau_s \gg \tau_h$. Thus $1/T_{2M} > 1/T_{1M}$.

Where the electronic relaxation times are short such that $T_1 = T_2$ the nuclear resonances will not be greatly broadened, and quite sharp lines may be obtained, but where the paramagnetic species have quite long electronic relaxation times such that $T_1 > T_2$, the nuclear resonance may be broadened to such an extent that they may be no longer detectable, or if so, only poorly resolved. The latter is often obtained with ions with an S ground state such as Mn(II), and Fe(II).

The detailed Bloembergen-Solomon equations have also been modified by Sternlicht to take into account anisotropic electronic g tensors.²⁷

(V) Effect of chemical exchange on relaxation times and contact shifts.

The line width of the recorded N.M.R. spectrum of a ligand complexed with a paramagnetic ion, and the shift obtained, can be

greatly modified if the ligand is taking part in a chemical rate process, such as exchanging with ligand in the bulk diamagnetic solution.

In the extreme limit of very slow exchange, or the weak pulse limit, two resonance lines will be obtained, corresponding to the paramagnetic and diamagnetic environments. The line width expression for the complexed species in this case contains an exchange contribution, and is given by Piette and Anderson²⁸ as

$$\frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{T_M} \quad \text{--- (16)}$$

where T_M is the co-ordination time of the ligand.

At the opposite extreme of very fast exchange, or the strong pulse limit, only an averaged line is obtained. At intermediate exchange rates the situation is more complex, the recorded line width depending on the rate of chemical exchange, T_{2M} and the contact shift in the complex.

The original Bloch equations were modified to take account of chemical exchange, first by Gutowsky et al.²⁹ then by McConnell³⁰, but the most useful treatment is that due to Swift and Connick³¹ which will now be considered in detail.

Considering exchange of a ligand between two environments, one paramagnetic and the other diamagnetic, then the general expressions for $1/T_{2p}$, the contribution to the line width arising from the interaction with the paramagnetic species, and $\Delta\omega$, the observed shift in resonance position of the ligand N.M.R. lines from the corresponding diamagnetic line positions are given by

$$\frac{1}{T_{2p}} = \frac{f}{\tau_M} \left[\frac{(1/T_{2M})^2 + 1/T_{2M}\tau_M + (\Delta\omega_M)^2}{(1/T_{2M} + 1/\tau_M)^2 + (\Delta\omega_M)^2} \right] \quad (17)$$

and

$$\Delta\omega = \frac{f\Delta\omega_M}{\tau_M^2 [(1/T_{2M} + 1/\tau_M)^2 + (\Delta\omega_M)^2]} \quad (18)$$

The subscript M refers to the complexed species and f is the fraction of the ligand complexed.

Swift and Connick simplified these expressions by considering four limiting conditions, and these are reproduced below and the effect of change in temperature discussed in each case.

Case A: $(\Delta\omega_M)^2 \gg (1/T_{2M})^2, (1/\tau_M)^2$, then

$$\frac{1}{T_{2p}} = \frac{f}{\tau_M} \quad (19)$$

$$\Delta\omega = \frac{f}{\tau_M^2 \Delta\omega_M} \quad (20)$$

In this case relaxation occurs through the change in precessional frequency and is rapid and $1/T_{2p}$ is controlled by the rate of chemical exchange. Thus increase in temperature will decrease τ_M , and hence both $1/T_{2p}$ and $\Delta\omega$ will increase with increasing temperature; this corresponding to the slow exchange limit. However $\Delta\omega$ will increase much faster than $1/T_{2p}$ and so resolution will improve with increase in temperature.

Case B: $(1/\tau_M)^2 \gg (\Delta\omega_M)^2 \gg 1/T_{2M}\tau_M$, and

$$\frac{1}{T_{2p}} = f\tau_M\Delta\omega_M^2 \quad (21)$$

$$\text{and } \Delta\omega = f\Delta\omega_M \quad (22)$$

In this case chemical exchange is rapid and $1/T_{2p}$ is controlled by the rate of relaxation through the change in precessional frequency. Again increase in temperature will decrease τ_M , but in this case the line width will decrease with increasing temperature, this corresponding to the fast exchange limit. Increase in temperature will have no effect on $\Delta\omega$, assuming f does not change. Thus resolution will improve with increasing temperature.

Case C: $(1/T_{2M})^2 \gg (\Delta\omega_M)^2, (1/\tau_M)^2$, and so

$$\frac{1}{T_{2p}} = \frac{f}{\tau_M} \quad \text{--- (23)}$$

$$\text{and } \Delta\omega = \frac{f \Delta\omega_M T_{2M}^2}{\tau_M^2} \quad \text{--- (24)}$$

Here relaxation by T_{2M} is fast, and $1/T_{2p}$ is controlled by the rate of chemical exchange. Increase in temperature will thus increase both $1/T_{2p}$ and $\Delta\omega$, but $\Delta\omega$ will increase much more rapidly, and so again resolution will improve with increasing temperature.

Case D: $1/T_{2M} \tau_M \gg (1/T_{2M})^2, (\Delta\omega_M)^2$, and thus

$$\frac{1}{T_{2p}} = \frac{f}{T_{2M}} \quad \text{--- (25)}$$

$$\text{and } \Delta\omega = f \Delta\omega_M \quad \text{--- (26)}$$

Here chemical exchange is rapid and $1/T_{2p}$ is controlled by the T_{2M} relaxation process. In this case the effect of increase in temperature will depend on the effects of temperature on T_{2M} , which in turn depends on the paramagnetic ion. Sternlicht et al.^{32b} found that for Mn(II)-Adenosine Triphosphate complexing, which is

a τ_r controlled system, T_{2M} increased with increasing temperature, whereas Luz and Meiboom^{26a} found with Co(II)-methanol complexes, a τ_s controlled system, that T_{2M} decreased with increasing temperature.

By choosing other limiting conditions, other reduced forms of the general Swift and Connick equation can be obtained but as they are essentially combinations of the four cases discussed above they are not considered here.

The McConnell and the Swift and Connick equations have been used by Pearson and others to determine exchange rates of ligands complexed with various ions in solution³³.

(VI) Applications

a. General

In the main, the most extensive use of contact shifts has been in the study of complexes of transition metal ions, mainly Ni(II) and Co(II), although important studies have also been made of other systems.

Whilst much of the work done has been on stable, isolable chelate compounds of known and fixed stoichiometry, and then mainly from the inorganic chemists point of view, one of the earliest studies of complex formation as distinct from solvation involved the weak complexes formed in solution between Co(II) and simple alcohols³⁴. In this study an external standard was used, and, after correcting for bulk susceptibility shifts using the

Dickinson³⁵ equation, it was found that the CH_2 groups α - and β - to the hydroxyl group were shifted downfield, and that the α -group was shifted more than the β - group. This behaviour is typical of a σ -delocalisation mechanism in which all the shifts are in the same direction and are rapidly attenuated along the chain. This study also showed that when complexing occurs the N.M.R. method of measuring bulk susceptibilities using the Dickinson equation cannot be used.

Where such weak complex formation occurs, especially with ions having fairly long electronic relaxation times, preferential line broadening can also occur, the degree of broadening of the signal similarly being attenuated along the carbon chain with distance from the complexing site³⁶.

Similar contact shift studies of the complexes of Ni(II) and Co(II) with various amino ligands³⁷ showed that where stable chelates can be formed in solution very large contact shifts (up to 200 p.p.m.) can be obtained, in both positive (high field) and negative (low field) directions. However, in this case the precise mechanism of the shifts could not be stated with certainty, as delocalisation of unpaired electron spin could have occurred through both σ - and π -bond systems, and since there also existed the possibility of pseudocontact shifts.

The contact shift phenomenon has also been applied in structural studies, being used by McDonald and Phillips³⁸ in their studies of complexing between Histidine and Co(II) . Here the extent of complexing was monitored by following the solvent HOD

peak, a broad shifted peak indicating poor complexing, a sharp unshifted peak indicating that all the Co(II) was complexed by the Histidine. The N.M.R. data also indicated four different types of complexes, stable in different pH ranges, ranging from a 1:1 complex bonding only through the -CO_2^- group at pH 3.5, to a tetrahedral 2:1 complex complexing through both nitrogens and not the CO_2^- group at pH's above 11.5. The most significant results of this study however was that beginning with DL Histidine, D-D, L-L, and D-L complexes could be recognised, and the greater stability of the D-L complex established, thus illustrating the sensitivity of the N.M.R. contact shift mechanism as a method of measuring relative stabilities of complexes in solution.

Similar pH studies of complex formation between glycyl peptides and Ni(II) have also been carried out³⁹, the contact shifts depending on pH, and on whether the peptide is positively or negatively charged. Li⁴⁰ has also used selective broadening by transition metal ions in studies of amino acids, esters and peptides as a method of distinguishing between an -SH group and an -S-S- linkage. Thus if Cu(II) is added and an -SH group is present, the Cu(II) is reduced to Cu(I) and no broadening occurs, whereas if Mn(II) is added, complexing occurs at the -SH group and the proton signals from groups α to the SH site are greatly broadened. If however an -S-S-linkage is present no reduction occurs, Cu(II) complexes at the amino group, selective collapse of signals α to the nitrogen and the amino hydrogens occurs, thus affording a method of distinguishing between cysteine (-SH) and cystine (-S-S-).

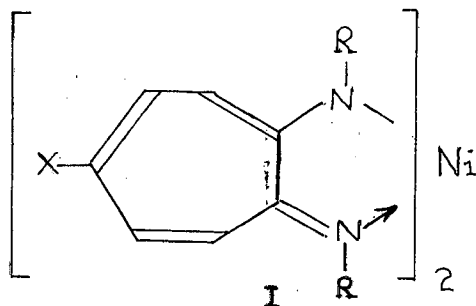
The greatest volume of work however has been done on chelates of fairly certain composition, Ni (II) and Co(II) being the ions mainly studied as they have fairly short electron spin relaxation times and hence give rise to spectra with quite small line widths.

This dependence of line widths on the electronic T_1 relaxation times has been shown by Eaton⁶ in his study of various paramagnetic acetylacetonate complexes. In this he obtained a correlation between the N.M.R. line widths in solution and qualitative E.S.R. characteristics; those ions which gave E.S.R. spectra at room temperature, and thus have large electronic T_1 's, gave the broadest N.M.R. line widths, whilst those ions which did not give E.S.R. spectra at liquid nitrogen temperatures gave moderately broad N.M.R. line widths.

The complexes which have received most attention so far fall into distinctive groups, being those with substituted aminotroponeimines, acetylacetonato type complexes, salicaldimine type complexes, and complexes with triarylphosphine or phosphoramidate ligands, and the application of the N.M.R. method will now be discussed in terms of these various groupings, including solvation number studies and electron transfer reactions.

b. Ni(II) aminotroponeimineate complexes

Probably the complexes most studied by the N.M.R. contact shift method have been those between Ni(II) and various substituted aminotroponeiminates of the type

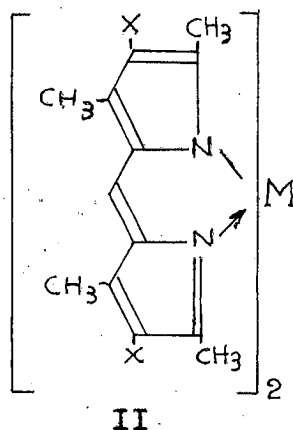


Eaton and his co-workers⁴¹ showed that for this system there exists in solution an equilibrium between the diamagnetic square planar and the paramagnetic tetrahedral forms, this intermolecular equilibrium giving rise to very sharp lines, which, due to the contact shift mechanism are well shifted in resonance position so facilitating complete analysis of the spectrum. Indeed, the line widths were in some cases so sharp as to allow the determination of first order hydrogen spin-spin coupling constants in aromatic substituents which, in a diamagnetic state, would give rise to prohibitively complex spectra. The work on these chelates have been extensively reviewed by Eaton and Phillips¹² together with early work on other systems and so only a brief account of the results is given here.

Since the distribution of the ligand about the Ni(II) ion is virtually symmetrical in both the square planar and tetrahedral states there is virtually no anisotropy in the Ni(II) electronic g tensors, and so pseudocontact shifts are practically non-existent. This, together with the fact that the delocalisation almost certainly occurs via a π -mechanism involving p_{π} - d_{π} bonding between the filled ligand p_{π} orbitals and the half filled Ni(II) d_{π} orbitals, has allowed the calculation of the magnitude and

signs of the hyperfine coupling constants for the various positions. When R and X in (I) are aromatic and are conjugated with the general system coupling constants for the different positions in these substituents have also been obtained. Knowledge of the signs and magnitude of these coupling constants have thus allowed the calculation and mapping of unpaired spin density throughout the whole molecule.

Also studied⁴² have been the bis-(pyromethene)-metal complexes of the type

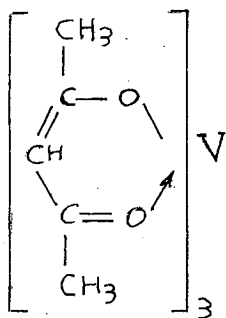


where $M = \text{Co(II)}$ and Ni(II) , in which the bonding to the metal ion is similar to that in the aminotroponimine complexes. Here too a π -transfer mechanism occurs leading to alternant contact shifts, but in this case delocalisation has been shown to occur not into the ligand bonding π -orbital but rather into a nonbonding π -orbital.

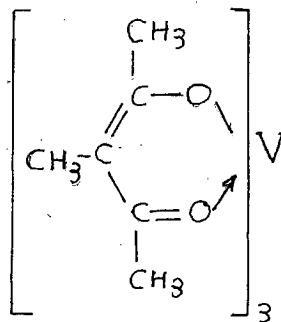
c. Acetylacetonato complexes

Acetylacetonato and benzoylacetonato complexes have been extensively studied, both as the tricomplex and as the dicomplex co-ordinated with other basic ligands. In their studies of

V(III)acetylacetonates Forman et al.⁴³ found that in the complexes



III



IV

the CH proton in (III) was shifted downfield whereas the corresponding C-CH₃ group in the 3-position in (IV) was shifted to high field, and hence concluded that delocalisation of unpaired electron spin occurred through a π -mechanism. This conclusion was also favoured by Eaton¹⁸ who concluded that the shifts arose from delocalisation through the ligand π -electron system and $d\pi$ - π bonding and back bonding, both metal to ligand and ligand to metal charge transfer processes occurring. However Luz, Silver and Fiat⁴⁴ in their ¹⁷O and ¹H studies of Mn(AA)₃, where AA is acetylacetonate, found that the very large ¹⁷O shifts could not be explained solely by delocalisation through the π -system, and concluded that the contact shift was predominantly due to delocalisation via σ -bonds. They also concluded that the ¹⁷O relaxation process occurred via the σ -bond system.

Horrocks et al.⁴⁵ in a study of the tris-acetylacetonato complexes of Co(II) and Ni(II) as the tetra-n-butylammonium cation, [nBu₄N][M(AA)₃], obtained the interesting result that for the Co(II) complex upfield shifts of the n-butyl peaks were obtained, whose position changed with addition of tetramethylammonium iodide.

Similar addition to a solution of the corresponding Ni(II) complex produced no change in the spectrum other than an increase in the intensities of the butyl resonances. The upfield shifts of the n-butyl protons in the Co(II) complex are due to pseudocontact shifts of opposite sign to those for the acetylacetonato group, no pseudocontact interaction occurring in the Ni(II) complex.

The pseudocontact shifts in the n-butyl group arise from ion pair formation in solution along the threefold symmetry axis in the complex. Similar conclusions have also been reached by La Mar⁴⁶ in a study of tetra n-butylammonium triphenylphosphine complexes of Ni(II) and Co(II). Thus pseudocontact interactions can be of great use in ion-pair formation studies.

Complexes between labile ligands and bis-acetylacetonato metal complexes provide a convenient system of known stereochemistry for studying the complexing behaviour of a great many ions. In this system the labile ligand co-ordinates in the trans position to give an octahedral complex, and quite detailed information about the method of electron delocalisation in the ligand can be obtained.

In an early study of this type of system, with pyridine and methyl pyridines complexed with Ni(II) and Co(II) acetylacetonates, Happe and Ward³ concluded that unpaired spin density reached the ligand position mainly through the σ -bonding system. That the sign of the methyl group shifts in methyl substituted pyridines were of opposite sign to the CH shift in the corresponding pyridine complex however led them to conclude that unpaired electron spin also reached the ligand π -system via an indirect σ - π interaction. They also concluded that pseudocontact effects were

significant in the Co(II) complexes but relatively non existent in the Ni(II) complexes, and introduced a convenient method of studying pseudocontact shift effects whereby corresponding Ni(II) and Co(II) complexes are studied and the Co(II) pseudocontact shifts obtained by normalising the Co(II) shift ratios until they correspond to the Ni(II) shift ratios. Thus by this method valuable information about the geometry of the complexes can be obtained.

Kluiber and Horrocks¹⁷ in a similar study of pyridine complexed with Ni(II) and Co(II) benzoylacetonato complexes, $M[-OC.(C_6H_5).CH.C(CH_3)_2-O-]_2$, obtained virtually the same shift ratios for the pyridine protons as Happe and Ward. For the Co(II) complex the shift ratios obtained were slightly different from those of Happe and Ward although qualitatively similar, and an interesting result obtained was that on complex formation spin decoupling of the α -pyridine proton occurred due to the relaxation effects of the unpaired electron on the metal ion, it showing as a broadened singlet, the β -protons thus showing as a doublet coupled only to the γ -proton.

Triarylphosphine and iso nitriles complexed with Co(II) and Ni(II) acetylacetonates have also been studied⁴⁷ and delocalisation through $d\pi - d\pi$ and $d\pi - P\pi$ bonding invoked to explain the results, any spin density in σ -orbitals concluded to be of only minor importance. Similar results have been obtained with azine-N-oxides and the corresponding azines complexed with Co(II) and Ni(II) acetylacetonates⁴⁸. The shifts obtained indicated electron spin density in the ligand π -orbitals, but the transfer mechanism

was uncertain, although with quinoline and isoquinoline, comparison with the corresponding N-oxides suggested that for the azines the spin was delocalised via a σ -mechanism^{48c}. In these studies calculation of the pseudocontact shifts for the Co(II) complexes relative to the Ni(II) complex as a function of the angle in the pseudocontact shift geometric term $(3\cos^2\chi-1)/r^3$ has been reported as indicating some degree of restricted rotation about the N-O bond.

However, in a later study of anilines complexed with $\text{Ni}(\text{AA})_2$, Kluiber and Horrocks⁴⁹ pointed out that in molecules such as aniline the nitrogen lone pair used in σ -bonding to the metal overlaps the ligand π -orbital system, and that delocalisation from the metal into the nitrogen σ -orbital can thus be transferred and distributed into the ligand π -system, so giving rise to a typical π -contact shift pattern for the ligand protons. They also suggest that this type of mechanism could account for the earlier results obtained with pyridine, picolines, amine-N-oxides, and triarylphosphines complexed with metal acetylacetonates. However, for ligands such as nitriles and isonitriles, where the single nitrogen lone pair orbital used for co-ordination is effectively orthogonal to the ligand π -system, and so does not overlap, such a mechanism would predict a σ -type distribution of electron spin density in contrast to the observed π -type distribution, and so a σ - π spin polarisation mechanism must be operating in these cases.

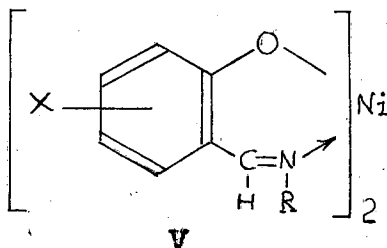
That the ratios of shifts are almost the same for dimethylaniline as for mono-methyl aniline indicates that the same delocal-

isation mechanism is operating for both these compounds, and hence ionisation of the NH proton cannot be occurring in this type of system, contrary to the suggestion of Thwaites and Sacconi⁵⁰ in their study of the Ni(II) complexes with Schiff bases formed from salicaldehydes and N,N substituted ethylene diamines.

Thus, while the contact shifts produced by complexing with paramagnetic ions can give useful information about spin density distribution in the ligand, caution must be used in interpreting the results in terms of delocalisation mechanisms.

d. Salicaldimine type complexes

A variety of salicaldimine type complexes with metal ions, mainly Ni(II) have been studied. Complexes of the type



have been studied by La Lancette⁵¹, Thwaites and Sacconi⁵⁰, and Holm and Chakravorty^{9,52}, in which a planar \rightleftharpoons tetrahedral equilibrium occurs similar to that in the Ni(II)-aminotroponimine complexes. Delocalisation of unpaired electron spin into the ligand π -system via metal-ligand $d\pi - p\pi$ bonding was invoked to explain the results obtained.

While the amount of electron spin delocalised in these systems is less than in the aminotroponimine complexes, similar behavior is shown in mixed complexes, the electron spin being de-

localised to different extents in the different ligands. As a different ligand is added to a solution of a symmetrical complex an equilibrium is set up between the two ligands and the complexed metal ion, and an asymmetric distribution of electron spin occurs, steric factors dependent on X and R determining the amount of spin delocalised within each ligand system.

Similar studies of the Ni(II) complexes with various o-hydroxy-naphtholdiimines⁵³ showed alternation in the signs of the contact shifts in agreement with valence bond structures, indicating a π - delocalisation mechanism. With bis-(pyrrole-2-aldimino) complexes with various metals, whilst the results indicated a planar \rightleftharpoons tetrahedral equilibrium, they could only be explained by both a π - and a σ -electron transfer, the σ -transfer system being of varying importance for different positions.

Results indicative of both a π - and a σ -transfer mechanism occurring simultaneously have also been obtained by Holm *et al.*⁵⁴ in a study of the bis-pyridine and bis-picoline complexes of NiI₂. Whilst calculation showed that pseudocontact shift effects were unimportant, the γ -proton shift in pyridine was of opposite sign to the γ -CH₃ shift in γ -picoline, indicative of a π -transfer mechanism; however the shifts of the α - and β -protons were not consistent with a π -mechanism.

e. Triarylphosphine and Hexamethylphosphoramide complexes

The triarylphosphine complexes of Ni(II) and Co(II) have been extensively studied by Horrocks and by La Mar,^{4,15,16b,46,55} and by

La Lancette and Eaton⁵, the complexes being of the types $[\text{Ar}_3\text{P}]_2\text{MX}_2$ and $[\text{nBu}_4\text{N}][\text{Ar}_3\text{PMX}_3]$, where $\text{M} = \text{Co(II)}$, Ni(II) and $\text{X} = \text{I}^-$, Br^- . Only in the Co(II) complexes were pseudocontact effects found to be significant, and the typical π -mechanism alternation in the signs of the shifts were obtained. Electron transfer reached the ligand π -bond system by $d\pi - d\pi$ overlap between the phosphorus and the metal and then by $\text{P}\pi - d\pi$ overlap between the phenyl ring and the phosphorus, the low electron spin densities found in the phenyl ring positions being due to poor $\text{P}\pi - d\pi$ overlap.

In these complexes the rate of exchange of the phosphorus ligand was found to vary according to the halide ion present in the complex, the bromide complex exchanging faster than the iodide, and the chloride complex faster than the bromide complex. This observed order of ligand mobilities has been explained⁵ as being determined by the strength of the metal-phosphorus $d\pi - d\pi$ bonding, this being partially compensated by halogen π -donation to the metal ion. The π -donation ability of the halides increase in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, leading to the strongest metal-phosphine bond, and so the slowest phosphine ligand exchange rate in the iodide complex. Consideration of σ -bonding by halide ions would however lead to the prediction of the inverse order of phosphine exchange rates as the electronegativity of the halide ions increase in the order $\text{I}^- < \text{Br}^- < \text{Cl}^-$. This halide π -donation explanation has also been favoured by Horrocks and Pignolet⁵⁵.

In their study of the Ni(II) and Co(II) halide complexes formed in the presence of excess triphenylphosphine they found that for a given halide ion the phosphine exchange rate is greater for the Ni(II) than for the Co(II) complex in direct contradiction to the order found by La Mar^{16b}. However, as they point out, La Mar used stoichiometric quantities of ligand, and hence the complexes would be very susceptible to solvolysis.

Hexamethylphosphoramide complexes have been studied by Wayland and Drago⁵⁶. When the halide ion is held constant and the metal ion varied their results give the order of increasing tendency toward co-valent bonding as Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II).

In their study of Co(II) complexes of the type CoL_2X_2 , where L is either pyridine or hexamethylphosphoramide and X is Cl^- , Br^- , or I^- , they found^{56b} that the extent of electron spin delocalisation from the metal to the neutral ligand is dependent on which halide ion is present in the complex. Delocalisation to the pyridine or hexamethylphosphoramide ligand was found to be greatest if iodide ion was present in the complex, somewhat less for the bromo- and least for the corresponding chloro- complex. This order is the same as for the order of phosphine ligand bond strengths in the triarylphosphine complexes with Co(II) and Ni(II) halides.

f. Solvation numbers and preferential solvation

Another use of the effects produced by paramagnetic ions has been in the determination of the solvation numbers of many ions, and in mixed solvents preferential solvation has been elucidated.

That solvation of a paramagnetic ion reduces relaxation times and produces an increase in the line widths of the solvating molecule has been used to determine the composition of the solvation shell in mixed solvents. Thus Fratiello and Christie⁵⁷ found that in a 1:1 pyridine-water solution Mn(II) produced extensive line broadening, especially of the water resonance, whereas Co(II) and Ni(II) broadened the pyridine lines more than the water line, $\alpha > \beta \gg \gamma$, thus indicating preferential solvation of Mn(II) by water and of Co(II) and Ni(II) by pyridine. In similar studies of Dioxan-water and Tetrahydrofuran-water systems Fratiello⁵⁸ found that only the water line was affected by added paramagnetic ions, and hence concluded that cyclic ethers do not undergo ion-dipole interaction in aqueous solution. However, it has also been reported⁵⁹ for dioxan-water mixtures of varying composition that while $\text{Mn}(\text{ClO}_4)_2$ indicated preferential solvation by water, with MnSO_4 , beyond a modest dioxan concentration, the line width of the water peak essentially decreased to the metal free value as the dioxan mole fraction increased. The suggested explanation for this is that ion pair formation between Mn^{2+} and SO_4^{2-} and preferential solvation by dioxan at the remaining co-ordinate positions in the ion pair occurred, this conclusion being qualitatively supported by the behavior of the dioxan resonance.

A somewhat similar study has been reported on the effect of Cr(III) complexes with non-labile inner co-ordination spheres on the ^{19}F N.M.R. of F^- and PF_6^- ions in aqueous solution⁶⁰ in which ^{19}F relaxation occurs mainly by ion association in the second co-

ordination sphere. In this study it was found that as the bulk of the Cr(III) complex increased so too did the ^{19}F line widths, indicating that the second co-ordination sphere water was more easily removed from a bulky complex to allow replacement by F^- or PF_6^- , the T_2 relaxation processes being controlled by dipolar interactions. This technique of outer sphere relaxation processes and the dependence on steric factors is a relatively new approach and holds out promise as a method of assessing relative steric hindrance at different positions within a molecule.

The contact shift produced in solvation of a paramagnetic ion has been utilised to determine the solvation numbers of various ions, both paramagnetic and diamagnetic. The diamagnetic shifts produced on solvation are very small, but if the exchange rate in the solvation shell is slow enough, then addition of a paramagnetic ion which has a very short solvation exchange time will shift the bulk water resonance, thus giving two peaks corresponding to the bulk solvent and the molecules in the solvation shell of the diamagnetic ion. This type of hydration study has been carried out directly by ^{17}O N.M.R.⁶¹, and using Co(II) to shift the bulk solvent resonance⁶² so enabling the relative intensities of the two peaks to be measured and hence the hydration number to be calculated knowing the concentration of diamagnetic ion and water. Temperature studies of such systems can also give information about exchange rates in the solvation sphere.

Such a method only gives approximate solvation numbers, being dependent on the accuracy with which the relative intensities

of the two sets of resonances can be measured. A more refined method is the "Molal shift" method developed by Alei and Jackson.⁶³ In this method the shift produced by the addition of paramagnetic ions is measured in the presence and the absence of the diamagnetic ion under study, and from these and the concentrations of diamagnetic ions and of the water in each solution the solvation number can be easily calculated.

Another more refined method of calculating solvation numbers utilising the strong relaxation effects produced by addition of Mn(II) and the perturbation produced by addition of diamagnetic ions is that due to Swift and Sayre⁶⁴ who developed an empirical expression allowing calculation of solvation numbers from data obtained from a single series of measurements. Both these methods depend on the fact that if a diamagnetic ion is added then there are effectively less solvent molecules present to interact with the paramagnetic ion and hence the effects produced by the paramagnetic ion will be effectively enhanced. Hydration of Ni(II) and VO^{2+} has also been studied by ^{17}O N.M.R.⁶⁵, the former by direct measurement of the bound water signal, and a series of paramagnetic ions studied by following the variation of shift and line width with temperature.⁶⁶

The strong relaxation effects produced by paramagnetic ions on solvent water have also been utilised in the study of metal binding in macromolecules such as RNA., DNA and ATP. Eisinger et al.⁶⁷ derived an enhancement factor relationship which enables the type of binding occurring to be determined. In this method relaxation times are measured in three solutions, one containing

both metal ion and binding molecule, one just the binding molecule, and the other pure water. By this method three different binding situations can be clearly distinguished; that binding occurs at an interior site inaccessible to solvent water, or at an exterior site accessible to water, or that binding does not occur. This technique has been used in the study of the formation of ternary enzyme-metal-substrate complexes in solution⁶⁸ and is clearly of importance in the study of biologically important systems. A somewhat similar series of relaxation time studies of complexing between paramagnetic ions and nucleic acids and A.T.P. in which binding occurs mainly at the phosphate group have been carried out by Sternlicht et al.^{25,32}.

Probably the most exhaustive solvation studies have been those of Luz and Meiboom^{26,69} on Ni(II) and Co(II) in methanol and methanol-water mixtures over a wide range of temperature. At low temperatures in methanol solution separate peaks were obtained for bound and bulk methanol, enabling co-ordination numbers to be crudely evaluated, and in the presence of added water mixed methanol-water complexes obtained, whose equilibrium constants were calculated, as were the enthalpy and entropy of exchange of methanol molecules in methanol complexes. Similarly obtained were hyperfine coupling constants for water, methanol OH and CH₃ groups, and study of the relaxation processes indicated that at low temperatures dipole-dipole interaction dominated the line widths, but that as the temperature increased methanol exchange began to contribute more and more to the line widths. Exchange of whole

molecules only occurred, proton exchange between the complexes and the bulk solution being unimportant, thus confirming Pearsons³³ conclusions. Another interesting result was that addition of very small amounts of water dramatically increased the rate of methanol exchange between the complexes and the bulk methanol.

g. Electron exchange in organic radicals

Hyperfine contact interactions between unpaired electrons and protons in organic anions and radicals have been studied by N.M.R., and information obtained on hyperfine coupling constants and spin density at different positions in the molecules⁷⁰. In these systems exchange of the unpaired electron between the anion and the corresponding neutral molecule occurs, and the situation is analogous to ligand exchange with a paramagnetic ion.

In studies of alkyl substituted aromatic species dramatic selective broadening of the aromatic ring protons relative to the alkyl protons has been observed^{70c}, and from the shifts observed the signs and magnitudes of the electron-proton hyperfine interaction constants calculated. Similarly rate constants for electron transfer have been obtained^{70a,b}.

One very interesting observation made in a study of electron exchange between quinones and the corresponding semiquinone^{70b} radicals was that, for the ethyl group in 2,5 diethoxyquinone, as T_2 for the CH_2 group decreased under the influence of an increasing concentration of the semiquinone radical, the CH_3 triplet approached closer and closer to a purely first order spectrum. A similar reversion to first order behavior was also shown by the methyl resonance in isopropylquinone.

PART 3. COBALT (II) COMPLEXES OF ALCOHOLS AND POLYHYDROXY
ALCOHOLS

(I) Introduction

Since the early work of Phillips, Looney and Ikeda³⁴ no really comprehensive study of complexes formed between alcohols and paramagnetic ions has been reported, although Pearson³³ has studied exchange rates of some simple alcohol ligands and various ions. In view of the potential use of the contact shift phenomenon as an aid in structural and configurational determination the complexes formed in solution between alcohols, polyols, and carbohydrate derivatives and cobalt have been studied.

Cobalt was chosen as the paramagnetic ion to study as due to its short electron relaxation time the degree of line broadening obtained at concentrations high enough to give fairly large averaged contact shifts is fairly small, so giving well resolved spectra.

The tetramethylammonium cation was chosen as the internal reference standard as, at the time, it was thought that due to its positive charge it would be less likely to be affected by cobalt ion than any neutral standard. However, the problems associated with this as an internal reference standard are considered later in section 3(V).

The use of this reference standard precluded the use of cobalt perchlorate as, at the high cobalt perchlorate concentrations required, tetramethylammonium perchlorate was virtually completely salted out from solution. It has however been successfully used

as an internal reference standard at much lower cobalt perchlorate concentrations⁷¹. Cobalt chloride was thus used as it was easily available, and, of the simple cobalt salts the least likely to form internal complexes in solution⁷².

The alcohols studied fall naturally into five groups; simple mono alcohols, simple diols, triols, straight chain polyols and carbohydrate derivatives, and the results are discussed in terms of these groupings, although some degree of overlap does occur.

(II) Experimental

(a) Experimental sample conditions

Except for the variable frequency and variable temperature studies, all spectra were recorded on pre-calibrated chart paper using a Perkin-Elmer model R10 60 Mc/s spectrometer, the probe temperature being 33.5°C.

Except where stated, all solutions were 1 molar in ligand and 0, 1, or 2 molar in cobalt chloride with 2% (0.18 molar) tetramethylammonium chloride as internal standard. The solutions were prepared in previously standardised 500 μ l graduated flasks, the ligand being weighed out and the tetramethylammonium chloride and cobalt chloride added using an "Agl" micrometer syringe from standard solutions in deuterium oxide. The solvent used was deuterium oxide and the standard tetramethylammonium chloride solutions used approximately 2.3 molar and the standard cobalt chloride solution approximately 2.9 molar.

The tetramethylammonium solution was standardised by weighing dried tetramethylammonium chloride and dissolving in deuterium oxide. After removal of water by repeated exchange with deuterium oxide by freezing and pump drying, the cobalt chloride was dissolved in deuterium oxide and the solution standardised gravimetrically by weighing the cobalt as $\text{Co}(\text{C}_5\text{H}_5\text{N})_4(\text{SCN})_2$ according to the method of Vogel⁷³.

The deuterium oxide molarities quoted were calculated by weighing the solution after making up to 500 μl , subtracting the combined weights of ligand, reference standard and cobalt chloride, then dividing the solvent weight in milligrams by 10 (assuming no water present). These may be regarded as an approximate measure of the solvent molarity.

In some cases of comparison of cobalt chloride and cobalt perchlorate with tert-butyl alcohol as reference standard, the paramagnetic salt and reference standard were weighed out together with the ligand for each individual solution. Such solutions are separately identified in the results section.

(b) Preparation of polyhydroxy alcohols

Potassium borohydride reductions were carried out according to the method of Carson et al.⁷⁴, and the products tested for the presence of free sugar by paper chromatography on Whatman No.1 paper using n Butanol/Ethanol/Water 4/1/5 top layer as eluant, the spots being developed by spraying with silver nitrate in acetone then sodium hydroxide in methanol⁷⁵.

Xylitol

Xylitol was prepared from D-Xylose by potassium borohydride reduction, yielding a syrup which crystallised on standing for four weeks at -5°C . Recrystallisation from absolute ethanol gave in 66% yield a product chromatographically free from free sugar. m.p. $92.5-93.5^{\circ}\text{C}$; Literature value⁷⁴ $93.0-94.5^{\circ}\text{C}$.

L-Arabitol

L-Arabitol was prepared from L-Arabinose by potassium borohydride reduction. Two recrystallisations from absolute ethanol gave in 55% yield a product chromatographically pure. m.p. $101.5-102^{\circ}\text{C}$. Literature value⁷⁶ 102°C .

L-Threitol

L-Threitol was prepared from D-(+)-diethyltartrate by potassium borohydride reduction. The crude product was purified by passage through Dowex LX2 ion exchange resin (40 ml.) in the hydroxyl form, eluting with water at the rate of 5 ml. fractions per 20 mins. Paper chromatography showed the early fractions to be pure and the later fractions slightly contaminated. Recrystallisation from absolute ethanol, seeding with some chromatographically pure material, gave in 24% overall yield a chromatographically pure material.

m.p. 88.5°C ; $[\alpha]_{\text{D}}^{20} + 13.2^{\circ}$ (c, 1.81 in EtOH).

Literature values⁷⁷ m.p. $88.5-89.5^{\circ}$; $[\alpha]_{\text{D}} + 13.1^{\circ}$.

L-Iditol

L-Sorbose was reduced by potassium borohydride and the crude product acetylated with acetic anhydride-anhydrous sodium acetate,

then the L-iditol and D-sorbitol hexa-acetates separated by the method of Gramer and Paesue⁷⁸. Paper chromatography on a paper impregnated with dimethyl sulphoxide, eluting with di-isopropyl ether, showed the L-iditol hexa-acetate to be free from D-sorbitol hexa-acetate, but the D-sorbitol hexa-acetate to be slightly contaminated.

Yield L-iditol hexa-acetate 28%. m.p. 121.5°C. $[\alpha]_D^{18} - 25.9^\circ$ (c, 2.32 in CHCl_3). Literature Values⁷⁸: m.p. 121.5°C $[\alpha]_D - 25.5^\circ$.

The L-iditol hexa-acetate was then catalytically de-acetylated with sodium in anhydrous methanol. Recrystallisation from absolute ethanol gave, in 80% yield,

L-iditol m.p. 73.5 - 74°C. $[\alpha]_D^{19} - 3.5^\circ$ (c, 4.2 in H_2O)

Literature Values⁷⁹: m.p. 73-74°C; $[\alpha]_D - 3.5^\circ$.

D-Talitol

D-Talitol was prepared from mannitol by $\text{S}_{\text{N}}2$ replacement of the 4-O-mesyl group in 3-O-benzoyl-4-O-mesyl-1,2;5,6-di-O-isopropylidene-D-mannitol by acetate ion.

1,2;5,6-di-O-isopropylidene-D-mannitol was prepared from D-mannitol by the method of Baer and Fischer⁸⁰ in 79% yield.

m.p. 119-120°C. Literature value⁸⁰: m.p. 122°C.

Without further purification the material obtained was benzoylated by the method of Sugihara and Yuen⁸¹, to give after two recrystallisations from absolute ethanol 3-O-benzoyl-1,2;5,6-di-O-isopropylidene-D-mannitol in 27% yield.

m.p. 106°C; $[\alpha]_D^{20} - 8.4^\circ$ (c, 2.61 in CHCl_3).

Literature values⁸¹: m.p. 106.5 - 107.5°C; $[\alpha]_D^{22} - 8.5^\circ$.

3-O-Benzoyl-4-O-mesyl-1,2;5,6-di-O-isopropylidene-D-mannitol

was then prepared by the method of Baker and Haines⁸² to give a pale yellow coloured oil which crystallised spontaneously on standing for three days. Recrystallisation from absolute ethanol yielded 3-O-benzoyl-4-O-mesyl-1,2;5,6-di-O-isopropylidene-D-mannitol in 52% yield. m.p. 74-75°C; $[\alpha]_D + 20.0^\circ$ (c, 2.50 in chloroform).

Literature values⁸²: m.p. 74-75°C; $[\alpha]_D + 13.9$ (no solvent given).

The product was then treated with anhydrous sodium acetate in dimethyl formamide containing about 0.5% water⁸² to give ultimately a yellow-brown amorphous mass. This crude produce was then de-benzoylated and de-acetylated with sodium in anhydrous methanol⁷⁷, and then after all the sodium ions had been removed by IR-120(H⁺) resin, excess IR-120(H⁺) resin added and the product de-isopropylidenated by shaking for one hour and then leaving over night. After filtering off the resin, the methanol was removed in vacuo to yield a brown coloured syrup which crystallised on standing for one week.

The crude D-talitol was then purified by passage through a column of 100 ml. de-acidite FF strong base resin in the hydroxyl form, eluting with de-ionised water at a rate of 5 ml. per 15 minutes. Removal of the water in vacuo at 45°C yielded a clear, colourless syrup which crystallised on standing for four weeks at -5°C. Recrystallisation from absolute ethanol yielded D-talitol in 53% yield based on 3-O-benzoyl-4-O-mesyl-1,2;5,6;di-O-isopropylidene-D-mannitol.

m.p. 88-89°C $[\alpha]_D + 3.4^\circ$ (c, 3.2 in water)

Literature values⁸¹: m.p. 88-89°C, $[\alpha]_D + 3.7^\circ$.

Separation of meso- and racemic-Butane-2,3-diols

The two isomeric diols in commercial butane-2,3-diol were separated by separation of their isopropylidene derivatives by fractional distillation and then hydrolysis. The isopropylidene derivatives were prepared by the method of Neish⁸³ in a total of 55% yield, gas liquid chromatographic analysis on a polyethylene glycoladipate column indicating about 70-75% threo-ketal.

Repeated fractional distillation through a 2 ft. column packed with Dixon gauze rings, with combination and final refractionation of the first, low boiling point fractions of each distillation, and of the residues eventually yielded four final fractions of composition as given below. The stillhead used was such as to return at least four-fifths of the distillate.

Fraction Type	G.L.C. Analysis	N.M.R. Analysis (CH peaks)	% Yield	B.P. Range
Threo ketal	92.5% threo	90.4% threo	14.8	109-111°C
Erythro ketal	88.1% erythro	84.8% erythro	5.2	119-119.5°C
Threo rich fractions	76.4% threo	72.8% threo	31.4	112-116°C
Erythro rich fractions	65.5% erythro	67.4% erythro	6.1	116-119°C

Literature boiling points⁸³: threo-ketal 109.5-110.5°C;
erythro-ketal 119°C.

Hydrolysis of the two ketals was carried out by adding two volumes of water containing the equivalent of 50 ml. conc. H₂SO₄ per litre.

Racemic-butane-2,3-diol was obtained from the threo-ketal by hydrolysis according to Neish⁸³ giving after distillation a 55% yield of racemic-butane-2,3-diol.

b.p. 177-178°C. m.p. di-p-nitrobenzoate 124-125°C.

Literature values: b.p.⁸⁴ 176°C. m.p. di-p-nitrobenzoate⁸⁴ 128°C.

Meso-butane-2,3-diol was similarly obtained in 64% yield on hydrolysis of the erythro-ketal.

b.p. 180.5-181.5°C. m.p. di-p-nitrobenzoate 187-188°C.

Literature Values: b.p.⁹¹ 181°C. m.p. di-p-nitrobenzoate⁸⁴ 188-189°C.

Preparation of cis- and trans-cyclic-1,2-diols.

Trans-hydroxylation of the appropriate cyclo-ene was in each case achieved by treatment with performic acid by the method of Cope et al.⁸⁵

Cis-hydroxylation was achieved by treatment with potassium permanganate at -30°C according to the method of Clark and Owen⁸⁶, the temperature being obtained by immersion in a methanol-solid carbon dioxide bath.

Trans-Cyclohexane-1,2-diol.

Trans-cyclohexane-1,2-diol was prepared from cyclohexene in 79% yield after recrystallisation from carbon tetrachloride.

m.p. 103-104°C: m.p. di-p-nitrobenzoate 127-128°C.

Literature values: m.p.⁸⁵ 103-104°C. m.p. di-p-nitrobenzoate⁸⁷ 129-129.5°C.

cis-Cyclohexane-1,2-diol

This was prepared from cyclohexene in 15% yield after recrystallisation from carbon tetrachloride.

m.p. 97°C . m.p. di-p-nitrobenzoate $147-148^{\circ}\text{C}$.

Literature values: m.p.⁸⁶ 98°C : m.p. di-p-nitrobenzoate⁸⁷ 149°C .

trans-Cyclopentane-1,2-diol

This was prepared from cyclopentene giving a yield of 18% after distillation in vacuo.

b.p. 150°C (14-15 m.m.) Hygroscopic solid.

m.p. di-p-nitrobenzoate $143-144^{\circ}\text{C}$.

Literature value:⁸⁸ m.p. di-p-nitrobenzoate 143°C .

cis-Cyclopentane-1,2-diol

This was prepared from cyclopentene giving a yield of 20% after distillation in vacuo.

b.p. $103-105^{\circ}\text{C}$ at 9-10 m.m. m.p. di-p-nitrobenzoate 113°C .

Literature values: b.p.⁸⁴ 98°C at 9 m.m.

m.p. di-p-nitrobenzoate 117°C ⁸⁸.

DL-1,4-anhydrothreitol

DL-1,4-anhydrothreitol was prepared by transhydroxylation of 2,5-dihydrofuran⁸⁹. After two distillations in vacuo 1,4-anhydrothreitol was obtained in 25% yield as a hygroscopic solid.

b.p. $164-167^{\circ}\text{C}$ at 15 m.m. m.p. di-p-nitrobenzoate⁹⁰ 203°C .

mixed m.p. with genuine sample⁹⁰ of di-p-nitrobenzoate 203°C .

2-C-deuteropropylene glycol

2-C-deuteropropylene glycol was prepared by lithium aluminium deuteride reduction of acetol acetate. Freshly distilled acetol acetate (1.21g., 10.4 m.M.) in 15 ml. dry ether (distilled from LiAlH_4) was added dropwise to a slurry of lithium aluminium deuteride (0.39g, 9.4 m.M) in 25 ml. dry ether with stirring. After stirring for 45 min. at room temperature the reaction mixture was heated under reflux for 1 hour, the condenser being protected from moisture throughout.

Wet ether was then added to decompose the excess of lithium aluminium deuteride, and then a solution of 3g. potassium carbonate in 4 ml. water added. After stirring for 15 mins. excess solid potassium carbonate was added until the slurry had set to an amorphous mass and then the ether removed in vacuo. The solid residue was then placed in a sohxlet thimble and extracted continuously with chloroform overnight. The chloroform was then removed in vacuo.

Yield 0.64g, 83% (crude) as a mobile very pale yellow oil.

The crude material was then used without further purification as its N.M.R. spectrum showed it to be virtually free from any secondary CH resonance.

(III) Results

The results in the following tables, unless otherwise stated, are referred to the tetramethylammonium ion as having a constant resonance position of 6.83τ . Such τ values can be converted to those relative to tert-butanol as internal reference standard by $+0.8\tau (\pm 0.1\tau)$ for 1M cobalt and $+2.0\tau (\pm 0.3\tau)$ for 2M cobalt. (see section 3(V)).

Unless otherwise stated, each set of results is the average of four scans of the spectrum. Further experimental details are given in section 3(II)(a).

Where the assignment of particular peaks is not obvious, they are labelled A, B, C ..., beginning with the peak at lowest field. Since the number of peaks is sometimes greater in 2M cobalt than in 1M cobalt solutions, corresponding peaks may sometimes be labelled differently in the two solutions.

Where line widths could not be measured with any degree of accuracy gaps are left in the appropriate table.

Table 1. Methanol

Conc. CoCl_2 <u>M</u>	τ	CH_3 $\Delta\nu$ 1/2 c/s	τ	OH $\Delta\nu$ 1/2 c/s	D_2O Conc. <u>M</u>
0	6.67	0.7	5.33	1.0	51.0
1	2.24	12.0	-3.46	54.0	50.5
2	-4.75	30.8	-13.86	105	49.8



Table 2. Ethanol

Conc. CoCl ₂ <u>M</u>	τ	CH ₃	τ	CH ₂	τ	OH	Conc. D ₂ O <u>M</u>
		ΔV 1/2c/s		ΔV 1/2c/s		ΔV 1/2c/s	
0	8.88	1.0	6.64	1.0	5.33	0.8	-
1	7.64	13.6	3.70	2.0	-4.10	59.3	50.3
2	5.76	16.8	-0.55	28.8	-14.14	97	48.7

Table 3. Propanol

Conc. CoCl ₂ <u>M</u>	τ	CH ₃	τ	β -CH ₂	τ	α -CH ₂	τ	OH	Conc. D ₂ O <u>M</u>
		ΔV 1/2c/s		ΔV 1/2c/s		ΔV 1/2c/s		ΔV 1/2c/s	
0	9.13	1.3	8.48	1.3	6.47	0.9	5.33	1.0	50.6
1	8.32	14.5	7.44	22.9	4.03	16.2	-4.36	60.0	49.5
2	7.08	-	5.72	26.9	-0.07	26.7	-14.75	121	47.2

Table 4. iso-propanol

Conc. CoCl ₂ <u>M</u>	τ	CH ₃	τ	CH	τ	OH	Conc. D ₂ O <u>M</u>
		ΔV 1/2c/s		ΔV 1/2c/3		ΔV 1/2c/s	
0	8.86	1.0	6.01	1.2	5.32	1.1	50.4
1	7.88	10.9	4.73	21.3	-4.47	62.2	49.4
2	6.39	15.4	2.66	27.6	-15.08	114	47.7

Table 5. n-butanol

Conc. CoCl ₂ M	α -CH ₂ $\Delta\nu$ τ 1/2c/s		β -CH ₂ $\Delta\nu$ τ 1/2c/s		γ -CH ₂ $\Delta\nu$ τ 1/2c/s		CH ₃ $\Delta\nu$ τ 1/2c/s		OH $\Delta\nu$ τ 1/2c/s		Conc. D ₂ O M
0	6.42	2.0	8.56 ^a		8.56 ^a		9.11		5.34	1.7	50.4
1	3.99	16.4	7.41		7.86		8.30	15.3	-4.35	54.9	-
2	-0.07	27.4	5.69	24.7	6.8 ^b		7.11		-13.59	103	49.6

(a) Very complex multiplet system. Shift taken as centre of multiplet system.

(b) Co-incident with the tetramethylammonium peak

Concentration of n-butanol in each solution only M/2 due to poor solubilityTable 6. sec-butanol

Conc. CoCl ₂ M	CH $\Delta\nu$ τ 1/2c/s		CH ₂ $\Delta\nu$ τ 1/2c/s		β -CH ₃ $\Delta\nu$ τ 1/2c/s		γ -CH ₃ $\Delta\nu$ τ 1/2c/s		OH $\Delta\nu$ τ 1/2c/s		Conc. D ₂ O M
0	6.27	2.2	8.53	3.4	8.86	1.6	9.12	2.7	5.33	1.7	51.9
1	5.04	19.7	7.59		7.93	13.5	8.31	15.0	-4.61	60	-
2	3.05	22	6.1		6.54		7.14		-14.31	101	48.9

Concentration of sec-butanol in each solution only M/2 due to poor solubilityTable 7. iso-butanol

Conc. CoCl ₂ M	CH ₂ $\Delta\nu$ τ 1/2c/s		CH $\Delta\nu$ τ 1/2c/s		CH ₃ $\Delta\nu$ τ 1/2c/s		OH $\Delta\nu$ τ 1/2c/s		Conc. D ₂ O M
0	6.64	1.8	8.31	3.0	9.13	2.3	5.34	1.8	51.4
1	4.56	12.3	7.38	21.1	8.29	11.1	-4.37	46	51.3
2	0.95	21.4	6.05		7.08		-14.46	114	49.8

Concentration of iso-butanol in each solution only M/2 due to poor solubility.

Table 8. tert-butanol

Conc. tBuOH·M	Conc. CoCl ₂ M	C·(CH ₃) ₃ τ	Δν 1/2c/s	OH τ	Δν 1/2c/s	Conc. D ₂ O M
0.18	0	8.77	0.8	5.32	1.6	—
1.0	1	7.91	5.1	-4.68	60.5	48.3
1.0	2	6.83 ^a		-15.03		45.5
0.28	0.99 ^b	7.97				51.0
0.31	2.01 ^b	6.83 ^a				49.2

(a) tert-butanol and tetramethylammonium peaks superimposed.(b) Solutions prepared by weighing out each component individually then dissolving in D₂OTable 9. Acetone

Conc. CoCl ₂ M	Acetone τ	Δν 1/2c/s	τ	OH Δν 1/2c/s	Conc. D ₂ O M
0	7.79	0.7	5.35	0.8	50.8
1	7.41	6.7	-4.50	60.9	49.5
2	6.83 ^a		-14.69		48.2

(a) Acetone and tetramethylammonium peaks coincident

Table 10. Dioxan

Conc. CoCl ₂ M	Dioxan τ	Δν 1/2c/s	τ	OH Δν 1/2c/s	Conc. D ₂ O M
0	6.28	0.5	5.35	0.8	—
1	5.77	6.5	-4.51	56.6	49.0
2	4.72	15.2	-15.08	98	47.3

Table 11. 2-methoxyethanol

Conc. CoCl ₂ <u>M</u>	α -CH ₂		β -CH ₂		OCH ₃		OH	Conc. D ₂ O <u>M</u>	
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.39 ^a		6.39 ^a		6.64	0.8	5.34	0.8	50.2
1	3.44	15.5	15.05	11.00	6.20	6.9	-4.52	62.2	48.9
2	-1.97	35.1	2.33	19.6	5.47	16.7	-14.92	110	47.2

(a) centre of A B spectrum. Analysis gives δ A - δ B1 = 8.8 c/s.

Table 12. Digol(2-(2-hydroxy)-ethoxyethanol)

Conc. CoCl ₂ M	α -CH ₂ τ	ΔV 1/2c/s	β -CH ₂ τ	ΔV 1/2c/s	OH τ	ΔV 1/2c/s	Conc. D ₂ O M
0	6.33	2.1	6.33	2.1	5.32	1.0	48.7
1	3.85	15.4	5.33	11.8	-5.28	67	47.9
2	-0.18	29.0	3.58	12.0	-16.16	138	—

Table 13. Cyclohexanol

Conc. CoCl ₂ M	Peak A τ	ΔV 1/2c/s	Peak B τ	ΔV 1/2c/s	Peak C τ	ΔV 1/2c/s	OH τ	ΔV 1/2c/s	Conc. D ₂ O M
0	8.3 ^a		8.7 ^a		8.7 ^a		5.35	0.9	52.6
1	5.16	21	7.5		7.9		-4.23	65	52.0
2	3.15	29	6.6 ^b		6.6 ^b		-14.43	113	50.6

Cyclohexanol only M/4 in all solutions due to poor solubility

(a) both peaks broad and τ values only approximate; $\pm 0.4 \tau$. CH peak probably too broad to be seen.

(b) tetramethylammonium peak superimposed on a very broad peak.

Table 14. Ethyleneglycol

Conc. Co(II) M	CH ₂ τ	ΔV 1/2c/s	OH τ	ΔV 1/2c/s	Conc. D ₂ O M	Standard used and value	Cobalt salt used
0	6.36	0.9	5.32	1.3		tBuOH as ^a	CoCl ₂
1	3.05	15.2	-3.32	61.9	49.9	8.77	
2	-2.08	33.9	-12.19	110	49.0		
1	2.18	14.9	-4.17	66.0	50.2	Me ₄ NCl as	CoCl ₂
2	-4.05	32.1	-14.23	108	48.9	46.83	
1	2.07	16.6	-3.43	56.2	47.6	tBuOH as ^a	Co(ClO ₄) ₂
2	-6.54	41.5	-15.91	114	43.2	8.77	

(a) tert-butanol added by weight to approx. 2%. All other additions from standard solutions.

Table 15. Propane-1,2-diol

Conc. Co(II) M	Co(II) salt used	Stand- ard used and τ value	Peak A $\Delta\nu$ τ 1/2c/s	Peak B $\Delta\nu$ τ 1/2c/s	Peak C $\Delta\nu$ τ 1/2c/s	CH ₃ $\Delta\nu$ τ 1/2c/s	OH $\Delta\nu$ τ 1/2c/s	Conc. D ₂ O M
N11	-	Me ₄ NCl as 6.83	6.58 ^a 0.8	6.58 ^a 0.8	6.14 0.9	8.88 0.8	5.32 0.8	
0.50	CoCl ₂	Me ₄ NCl as 6.83	3.86 23.6	5.22 ^b 11.5	5.22 ^b 11.5	8.32 8.9	0.77 33.5	49.8
1.00			0.18 ^c 25.3	3.08 ^c 25.3	3.97 ^c 23.9	7.45 8.7	-4.23 61.9	49.2
1.50			-4.76 44.6	0.50 32.1	2.29 30.9	6.37 14.0	-9.52 87	48.0
2.00			-10.35 58	-2.53 41	0.30 37	5.10 16.1	-14.58 125	47.7
1.00	CoCl ₂	Me ₄ NCl as 6.83	-0.17 29.1	2.90 24.9	3.83 23.7	7.38 10.2	-4.52 60	49.0
2.00			-10.63 56	-2.68 37	0.21 35	5.03 16.6	-14.62 99	48.4
1.00	CoCl ₂	Me ₄ NCl as 6.83	-0.25 34	2.85 26	3.83 24.9	7.36 10.5	-4.77 74	49.2
1.00	CoCl ₂	Me ₄ NCl as 6.83	-0.47 34.6	2.73 26.5	3.75 25.1	7.30 10.8	-4.98 72	49.8
0.48	CoCl ₂	Me ₄ NCl as 6.83	3.89 22.6	5.23 ^b 18.3	5.23 ^b 18.3	8.32 8.6	0.86 32.7	49.6
1.02			0.00 33.0	2.99 26.6	3.90 24.8	7.43 10.2	-4.44 62.6	
1.50			-4.53 47.1	0.56 31.0	2.34 28.3	6.39 12.3	-9.39 89	48.3
1.99			-10.07 53	-2.34 37.4	0.42 36.9	5.17 15.8	-14.39 107	47.3
0.50	CoCl ₂	tBuOH as 8.77	4.03 41	5.49 ^b 30.0	5.49 ^b 26.6	8.61 10.2	0.89 76	49.4
1.08			0.63 41	3.74 30.0	4.69 26.6	8.21 10.2	-3.66 76	48.9
1.53			-3.80 41	1.71 46	3.58 40	7.69 18.9	-8.39 103	48.4
2.00			-9.22 41	-0.86 45	2.15 36	7.02 18.9	-13.02 134	47.3
0.51	Co(ClO ₄) ₂	tBuOH as 8.77	3.80 25.1	5.42 ^b 24.2	5.42 ^b 24.2	8.58 13.6	0.89 64	48.0
1.00			-0.17 ~55	3.45 30.6	4.48 29.4	8.12 13.6	-3.64 134	46.3
1.52			-7.1 48	0.54 48	2.80 43	7.31 19.0	-9.31 ~190	43.6
2.04			-3.19 65	-3.19 65	0.48 60	6.18 28.2	-15.05 ~235	42.1

(a) Average of two peaks shown by CH₂ group at 6.66 τ and 6.50 τ .

(b) Both identical. A:(B + C) = 1:2.

(c) A=B=C=1 proton.

(d) All solutions with tBuOH as standard were weighed out. CoCl₂·6H₂O and Co(ClO₄)₂·6H₂O being used, and hence D₂O molarity is moles D₂O added plus moles H₂O added with Co salt. tBuOH 2%, about 0.3 M.

All solutions with Me₄NCl as standard were prepared using standard CoCl₂ solutions, each block of results corresponding to a different CoCl₂ solution.

Table 16. 0.5 M Propane-1,2-diol

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		CH ₃		OH		Conc. D ₂ O M
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0.50	3.85	26.6	5.23	18.0	5.23	18.0	8.32	9.0	0.73	35	51.7
1.00	0.37	30.0	3.16	27.4	4.02	24.9	7.48	10.3	-4.09	61.4	51.0

Table 17. 2-C-deuteropropane-1,2-diol

Conc. CoCl ₂ M	Peak A		Peak B		CH ₃		OH		Conc. D ₂ O M
	τ^a	$\Delta\nu$ 1/2c/s	τ^a	$\Delta\nu$ 1/2c/s	τ^a	$\Delta\nu$ 1/2c/s	τ^a	$\Delta\nu$ 1/2c/s	
0	6.52	2.6	6.52	2.6	8.88	2.6	5.28	0.9	50.0
1 ^b	-0.13	40	3.37	27.4	8.13	12.0	-4.47	72	49.6
2	-11.2		-1.78	45	6.72	23.1	-14.41		48.7

(a) τ values referred to t-butanol as 8.77 τ .

Concentration of diol perhaps uncertain as prepared product used without first redistilling.

(b) Addition of propane-1,2-diol and re-running gave a spectrum with peaks at -0.10, 3.42, and 4.52, the latter being of lower intensity than the others, and the CH₃ peak at 8.13.

Table 18. Propane-1,3-diol

Conc. CoCl ₂ M	OCH ₂		CH ₂		OH		Conc. D ₂ O M
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.34	0.9	8.24	1.4	5.31	0.9	-
1	1.58	37.7	7.30	20.6	-4.38	65	49.0
2	-5.95	67	5.83	26.6	-14.58	94	47.9

Table 19. Butane-1,3-diol

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		Peak D		Peak E		OH	Conc. D ₂ O M	
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0 ^d	6.20 ^a	1.4	6.20 ^a	1.4	6.20 ^a	1.4	8.31 ^b	1.3	8.82 ^c	0.9	5.32	1.5	49.6
1 ^d	0.58	65	2.64	31.1	3.47	29	7.3		7.50		-4.71	70	48.7
2	-9.49	97	-3.54	46	-1.07	43	5.39	20	5.39	20	-15.24	117	47.5

(a) Average of OCH at 6.07 τ and OCH₂ at 6.33 τ .

(b) CH₂

(c) CH₃

(d) A=B=C=1 proton, Probably D=2(CH₂) and E = 3(CH₃).

Table 20. Butane-1,4-diol

Conc. CoCl ₂ M	OCH ₂		CH ₂		OH		Conc. D ₂ O M
	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	
0	6.40	0.9	8.43	1.0	5.31	0.9	48.8
1	3.77	16.6	7.32	13.2	-5.04	75	48.3
2	-0.71	30	5.44	19.0	-16.11	137	—

Table 21. meso-butane-2,3-diol

Conc. CoCl ₂ M	CH		CH ₃		OH		Conc. D ₂ O M
	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	
0	6.31		8.89	1.2	5.31	0.9	49.0
1	3.26	21.1	7.81	10.3	-5.09	69	48.6
2	-2.52	37.7	6.09	17.0	-16.19	139	46.9

Table 22. racemic-butane-2,3-diol.

Conc. CoCl ₂ M	CH		CH ₃		OH		Conc. D ₂ O M
	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	
0	6.39		8.89	1.0	5.31	0.9	49.5
1	1.97	32.2	5.33	14.2	-4.89	74	49.1
2	-4.87	62	-0.17	24.0	-15.86	139	47.9

Table 23. trans-cyclohexane-1,2-diol

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		Peak D		OH		Conc. D ₂ O M
	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	τ	ΔV 1/2c/s	
0	6.66 ^a		8.1		8.4		8.8		5.31	0.9	48.1
1 ^b	3.87	28.0	6.05	16.5	7.16		7.74	20.6	-5.28	79	47.9
2 ^b	-0.37	51	2.56	20.7	5.7		6.21		-16.55	123	46.7

(a) A = 2H. Peaks B, C and D overlapping.

(b) A = B = 2 protons. Probably C = 2, D = 4 protons.

Table 24. cis-cyclohexane-1,2-diol

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		Peak D		OH		Conc. D ₂ O M
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0 ^a	6.23	10.6	8.52	12.9	8.52	12.9	8.52	12.9	5.32	0.9	48.0
1 ^b	1.43	34.2	6.83	8.2	7.83	9.4	7.83	9.4	-5.26	66	47.7
2 ^c	-6.82	69	4.12	30	6.83	20.4	7.62		-16.54	137	46.2

(a) A = 2 protons, C = 8. (b) A = 2 protons. Probably B = 2: C = 6 protons: Peak B coincident with tetramethylammonium peak. (c) A = B = 2 protons. Probably C = 4, D = 2 protons. Peak C coincident with tetramethylammonium peak.

Table 25. Technical butane-2,3-diol (unresolved, contains both meso- and racemic diols)

Conc. CoCl ₂ M	Peak A (= 1H)		Peak B (= 1H)		Peak C (= 3H)		Peak D (= 3H)		OH		Conc. D ₂ O M
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.35		6.35		8.89		8.89		5.31	0.9	49.5
1	1.97	36	3.38	23.7	5.35	18.0	7.83	13.9	-4.91	69	48.5
2	-4.80	53	-1.99	36	-0.11	24	6.19	17.1	-15.82	112	47.6

Integration of both CH and CH₃ peaks against each other indicates an approximately 1:1 mixture.

Table 26. M/2 cis-plus M/2 trans-cyclohexane-1,2-diols

Conc. CoCl ₂ <u>M</u>		Peak A $\Delta\nu$ τ 1/2c/s	Peak B $\Delta\nu$ τ 1/2c/s	Peak C $\Delta\nu$ τ 1/2c/s	Peak D $\Delta\nu$ τ 1/2c/s	Peak E $\Delta\nu$ τ 1/2c/s	Peak F τ	Peak G τ	Peak H τ	OH τ	$\Delta\nu$ 1/2c/s	Conc. D ₂ O <u>M</u>
1 ^a	1.56	33	3.83	27	6.06	20.2	7.17		7.79	20.2		47.5
2 ^b	-6.32	69	-0.25	57	2.68	21.6	4.20	30.5	5.8		6.4 6.7 7.3	46.9
										-5.35	74	
										-16.36	135	

(a) cis:trans ratio by weighing = 1:1.02 and measured by integration 1:1.01
(b) cis:trans ratio by weighing = 1:0.96 and measured 1:1.01

Table 27. trans-cyclopentane-1,2-diol

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		OH		Conc. D ₂ O M
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.02		8.3		8.3		5.32	1.6	49.2
1	4.88	13.7	7.43	24			-5.37	76	48.0
2 ^a	3.08	22.3	5.8		6.24		-16.40	145	47.3

(a) Probably A = B = 2 protons, C = 4.

Table 28. cis-cyclopentane-1,2-diol.^a

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		Peak D		OH	
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s
0	6.00		8.3		8.3		8.3		5.30	0.9
1	-3.56		5.99	27	7.34	13.6			-5.14	81
2 ^b	-18.26		2.66	28.7	5.35		5.98		-16.6	

(a) Actual concentration of diol not known with certainty as it is very hygroscopic even on slight exposure to the atmosphere.

(b) Diol-Me₄NCl-CoCl₂ soln. exchanged twice with D₂O by removing solvent in vacuo over P₂O₅ and then finally drying over P₂O₅ in vacuo at boiling acetone temperature in order to reduce HOD peak so enabling peak A to be seen clearly. Both peak A and HOD peaks overlapping, and HOD peak assigned to the apparently broadest peak.

Table 29. 1,4-anhydroerythritol

Conc. CoCl ₂ <u>M</u>	Peak A (2H)		Peak B (2H)		Peak C (2H)		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	5.70		6.05		6.34		5.32	0.9	49.7
1	2.64	18.9	4.97		5.41		-4.99	63	49.1
2	-3.06	39	2.75	29	3.61	31	-15.77	123	48.2

Table 30. DL-1,4-anhydrothreitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	5.8		6.2		6.2		5.31	0.9	49.6
1	4.57	9.6	5.37	35.5			-5.85	67	48.8
2	2.90	17.5	3.9		4.3		-16.08	132	48.4

Table 31. Glycerol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.39	0.9	6.39	0.9	6.39	0.9	5.31	1.2	50.2
1	2.20	30.1	3.09	29.7	4.08	21.5	-4.39	73	49.1
2 ^a	-4.28	43	-2.17	40	0.57	35	-14.50	117	47.8

(a) A = B = 2 protons, C = 1 proton

Table 32. Butane-1,2,4-triol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		Peak D		Peak E		OH	Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	
0 ^a	6.4	1.4	6.4	1.4	6.4	1.4	6.4	1.4	6.33	1.7	5.32	0.9
1 ^b	1.72	39	3.03		3.4				6.8		-4.54	67
2 ^c	-6.06		-5.0		-2.54	69	-1.10	39	4.59	51	-14.93	113

(a) Protons on C₁, C₂ and C₄ all overlapping. 6.4 taken as centre of multiplet structure

(b) Probably A = 2H; B = 2H, c = 1H. Peak E coincident with tetramethylammonium peak.

(c) Probably A = B = 1 proton, C = 2, D = 1, E = 2 protons. Peak C almost on the point of splitting into 2 peaks.

Table 33. Erythritol

Conc. Erythritol <u>M</u>	Conc. CoCl ₂ <u>M</u>	PEAK A		PEAK B		PEAK C		OH		Conc. D ₂ O <u>M</u>
		τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
1.0	0	6.33	2.6	6.33	2.6	6.33	2.6	5.30	1.3	49.4
1.0 ^a	1	2.28	25.7	3.48	31.1			-4.60	80	48.2
1.0 ^b	2	-5.0		-4.6		-1.83	55	-15.30	128	46.1
0.25 ^a	1.0	2.60		3.71		-	-	-4.11		52.3
0.51 ^a	1.0	2.55		3.67		-	-	-4.11		50.7
0.75 ^a	1.0	2.39		3.53		-	-	-4.52		48.9
1.0 ^a	1.0	2.28		3.45		-	-	-4.65		47.7

(a) A = 2, B = 4 protons.

(b) A = B = C = 2 protons.

Table 34. L-Threitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.35	2.8	6.35	2.8	6.35	2.8	5.30	1.7	49.4
1 ^a	2.3		2.7		3.32		-4.36	82	48.0
2 ^a	-4.37		-3.32		-1.95		-15.29	140	46.0

(a) A = B = C = 2 protons.

Table 35. D-Ribitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		Peak D		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.28	2.6	6.28	2.6	6.28	2.6	6.28		5.29	1.6	48.7
1 ^a	1.52	34.3	2.66	32.6	3.36		3.98	21.4	-4.66	79	47.4
2 ^a	-6.12	68	-3.44	61	-2.17		0.09	38	-15.02	136	45.9

(a) A = B = D = 2, C = 1 proton.

Table 36. Xylitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		Peak D		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.31	1.4	6.31	1.4	6.31	1.4	6.31	1.4	5.30	2.5	49.0
1	1.38		2.14						-4.47	46.5	47.7
2	-7.76		-5.21		-4.58		-3.73		-15.12	125	45.5

Table 37. L-Arabitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		Peak D		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.27	1.2	6.27	1.2	6.27	1.2	6.27	1.2	5.29	0.9	
1 ^a	0.67		1.75		2.30		3.09		-5.32	82	47.1
2 ^b	-7.5		-5.59	103	-3.59	69	-1.94	62	-14.30	129	45.2

(a) D = 2, (B+C+A) = 5 protons. Probably A = 1, B = C = 2 protons.

(b) Probably A = 1H, B = C = D = 2 protons.

Table 38. Allitol

Conc. CoCl ₂ <u>M</u> ²	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0 ^a	6.24	3	6.24	3	6.24	3	5.31		—
1 ^b	0.15	35	2.49	32.8	3.86	18.8	-4.61	92	—
2 ^b	-6.89	63	-3.39	58	-0.13	48.0	-14.92	126	—

(a) Reference solution only about 0.1M in Allitol; other solutions 1M.

(b) A = B = 2 protons, C = 4 protons.

Table 39. D-Sorbitol

Conc. CoCl ₂ <u>M</u> ²	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.29		6.29		6.29		5.28	1.1	47.6
1	~1.1		2.21	63	3.39		-3.85	79	45.6
2 ^a	-6.96		-5.40		-2.56		-15.28	130	45.1

(a) C = 2 protons. Probably A = 2, B = 4 protons

Table 40. L-Iditol

Conc. CoCl ₂ <u>M</u> ²	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	
0	6.30	7.1	6.30	7.1	6.30	7.1	5.29	3.5	
1 ^a	0.87	37	2.07		2.65		-4.52	66	46.5
2 ^a	-8.84	63	-4.77		-3.65		-14.82	112	45.1

(a) A = 2 protons. Probably B = 2, C = 4 protons.

Table 41. Dulcitol

Conc. CoCl ₂ <u>M</u> ²	Peak A		Peak B		OH	
	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s
0	6.29	1.7	6.29	1.7	5.32	0.9
1	1.84		2.66		-4.91	66
2	-5.56	75	-3.26	57	-15.46	117

In all cases the concentration of Dulcitol was only about 0.3M, being a saturated solution at room temperature.

Table 42. D-Mannitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	
0	6.25	1.9	6.25	1.9	6.25	1.9	5.29	0.9	47.6
1	1.08		1.95		3.44	25.5	-4.71	84	46.5
2	-7.50		-5.35	45	-1.43	51	-14.44	130	44.1

Table 43. D-Talitol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B	Peak C	Peak D	Peak E		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu_{1/2c/s}$	τ	τ	τ	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	
0	6.27		6.27	6.27	6.27	6.27		5.28	0.9	47.5
1	-0.23	43	1.09	1.7	2.17	3.17		-6.26		45.8
2 ^a	-10.33	71	-7.22	-5.68	-4.53	-1.91	50	-17.92	157	—

(a) Probably A = B = E = 1 proton.

In the tables following, the peaks are listed only in order of increasing values, and not with respect to origin.

Table 44. myo-inositol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	
0	5.94		6.45				5.29	4.2	48.4
1	4.93		5.1		5.5		-5.41	93	47.6
2 ^a	2.25		2.95		3.90		-16.51	129	47.0

(a) A = B = C = 2 protons.

Table 45. epi-inositol

Conc. CoCl ₂ <u>M</u>	Peak A		Peak B		Peak C		OH		Conc. D ₂ O <u>M</u>
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	
0 ^a	5.95		6.27		6.48		5.32	0.9	—
1 ^b	1.35	90	3.56	90			-4.38	77	48.2
2 ^c	-7.00	170	-0.13	137			-14.60	168	47.0

(a) Solution only about 0.1M in epi-inositol. (b) Solution 0.8M in epi-inositol:

Probably A = 4, B = 2 protons.

(c) Solution 0.8M in epi-inositol.

Table 46. D-Ribose

Conc. CoCl ₂ M	Peak A τ	Peak B $\Delta\nu$ 1/2 c/s	Peak C $\Delta\nu$ 1/2 c/s	Peak D $\Delta\nu$ 1/2 c/s	Peak E $\Delta\nu$ 1/2 c/s	Peak F τ	Peak G τ	OH $\Delta\nu$ 1/2c/s	Conc. D ₂ O 2M
0	4.78 ^a	5.09 ^b	5.93	6.23	6.47			5.31 2.8	49.3
1	1.17	1.76	2.75	3.28	4.07	4.61	5.33	-4.23 60	
2	-4.90	-1.35 34	0.72 54	2.14 32	3.33 30			-14.82 102	46.8

(a) α -anomeric proton: (b) β -anomeric proton

Table 47. L-Arabinose

Conc. CoCl ₂ M	Peak A τ	Peak B τ	Peak C τ	Peak D τ	Peak E τ	Peak F τ	OH $\Delta\nu$ 1/2c/s	Conc. D ₂ O 2M
0	4.79 ^a	5.50 ^b	6.2 ^c				5.29 1.6	48.6
1	3.81	4.21	4.59	5.20 14.7			-5.03 72	48.1
2	0.00	0.87	2.4 ^d	2.8 ^d	3.37	3.89	-16.28 134	47.7

(a) α -anomeric proton: (b) β -anomeric proton: (c) ring proton region; all peaks within ± 0.25 of 6.2 (d) peaks very small and broad. Intensity of the sum of (A + B) approximately one proton.

Table 48. D-Xylose

Conc. CoCl ₂ $\frac{M}{M}$	Peak A τ	ΔV 1/2c/s	Peak B τ	Peak C τ	Peak D τ	Peak E τ	τ	OH ΔV 1/2c/s	Conc. D ₂ O $\frac{M}{M}$
0	4.83 ^a		5.44 ^b	6.09	6.36	6.64	5.32	1.6	49.5
1 ^c	4.22		4.61	5.3	5.58		-4.75	61.75	47.6
2	3.34	27	3.88	4.57	4.9		-15.22	124	45.6

(a) α -anomeric proton: (b) β -anomeric proton: (c) (A + B) \approx 1 proton, (C + D) \approx 5 protonsTable 49. Methyl α -D-Xylopyranoside

Conc. CoCl ₂ M	Peak A τ	Peak B $\Delta\nu$ 1/2c/s	Peak C τ	Peak D τ	OMe $\Delta\nu$ 1/2c/s	OH $\Delta\nu$ 1/2c/s	Conc. D ₂ O 2M
0	5.25 ^a	4	6.44				47.9
1	4.76	7.9	5.4	5.6	5.81	6.04	47.4
2	3.7	4.02	17	4.2	4.94	5.19	45.6

(a) Anomeric proton.

Table 50. D-Lyxose

Conc. CoCl ₂ <u>M</u>	Peak A ΔV τ 1/2c/s	Peak B ΔV τ 1/2c/s	Peak C ΔV τ 1/2c/s	Peak D τ	Peak E ΔV τ 1/2c/s	OH ΔV τ 1/2c/s	Conc. D ₂ O <u>M</u>
0	5.01 ^a	1.5	5.15 ^b	2.7	6.19	5.33	47.9
1	3.44	13.7	4.14	11.1	4.89	-4.64	47.1
2	0.42	70	2.6	2.88	34	3.78	46.4

(a) α -anomeric proton.(b) β -anomeric protonTable 51. D-Glucose

Conc. CoCl ₂ <u>M</u>	Peak A ΔV τ 1/2c/s	Peak B ΔV τ 1/2c/s	Peak C τ	Peak D ΔV τ 1/2c/s	Peak E τ	OH ΔV τ 1/2c/s	Conc. D ₂ O <u>M</u>
0	4.79 ^a	5.4 ^b	6.23	6.43	6.59	5.27	47.7
1 ^d	4.36	4.59	13.7	5.24	5.66	-4.70	46.9
2 ^e	1.93 ^c	57	3.40	3.9	4.27	-14.83	45.7

(a) α -anomeric proton.(b) β -anomeric proton

(c) Peak A is just on the point of resolving into two separate peaks, 1.93 being the average of the whole mass.

(d) Probably (A + B) = 3, (C + D) = 4 protons

(e) Probably A = 2, (B + C + D) = 5 protons.

Table 52. methyl α -D-Glucopyranoside

Conc. CoCl ₂ <u>M</u>	Peak A ΔV τ 1/2c/s	Peak B ΔV τ 1/2c/s	Peak C ΔV τ 1/2c/s	Peak D τ	OMe ΔV τ 1/2c/s	OH ΔV τ 1/2c/s	Conc. D ₂ O <u>M</u>
0	5.21 ^a	6.23	6	6.42	3.0	6.60	-
1 ^b	4.74	15.7	5.58	19.3	6.05	7.0	46.6
2 ^c	1.9	2.2	3.7	4.21	5.20	14.8	45.8

(a) Anomeric proton.

(b) A = 3, B = 4 protons.

(c) (A + B) = 2 protons, (C + D) = 5 protons.

Table 53. Methyl- β -D-Glucopyranoside

Conc. CoCl ₂ <u>M</u> ²	Peak A $\Delta\nu$ τ	1/2c/s	Peak B $\Delta\nu$ τ	1/2c/s	Peak C $\Delta\nu$ τ	1/2c/s	Peak D τ	OMe $\Delta\nu$ τ	1/2c/s	OH $\Delta\nu$ τ	1/2c/s	Conc. D ₂ O <u>M</u>
0	5.64 ^a	2.3	6.2		6.60	5.3		6.45	1.5	5.34	2.7	47.3
1 ^b	4.68	13	4.96		5.75			5.88		-4.98	58	45.9
2 ^c	1.76	34	2.58	30	4.1		4.32	5.02	17.8	-15.47	120	44.0

(a) Anomeric proton

(b) A = 2, B = 1, C = 4 protons.

(c) Probably A = B = 1 proton, (C + D) = 5 protons

Table 54. D-Mannose

Conc. CoCl ₂ <u>M</u> ²	Peak A $\Delta\nu$ τ	1/2c/s	Peak B $\Delta\nu$ τ	1/2c/s	Peak C $\Delta\nu$ τ	1/2c/s	Peak D $\Delta\nu$ τ	1/2c/s	Peak E τ	Peak F τ	Peak G τ	OH $\Delta\nu$ τ	1/2c/s	Conc. D ₂ O <u>M</u>
0	4.84 ^a	2.6	5.13 ^b	1.7	6.09		6.22		6.46			5.30	1.7	49.2
1	3.86		4.17	17.6	4.6		5.28	15.9	5.6			-4.71	59	47.3
2	0.72	43	1.55	43	2.08	26	2.70		3.30	4.1	3.80	-14.91	117	47.0

(a) α -anomeric proton

(b) β -anomeric proton.

Table 55. Methyl α -D-Mannopyranoside

Conc. CoCl ₂ <u>M</u> ²	Peak A $\Delta\nu$ τ	1/2c/s	Peak B $\Delta\nu$ τ	1/2c/s	Peak C $\Delta\nu$ τ	1/2c/s	Peak D τ	OMe $\Delta\nu$ τ	1/2c/s	OH $\Delta\nu$ τ	1/2c/s	Conc. D ₂ O <u>M</u>
0	5.26 ^a		6.11		6.21		6.36	6.61	0.9	5.34	2.4	47.7
1 ^b	4.5		4.60	~21	5.40	16.2		5.97	6.7	-4.87	63	47.1
2 ^c	1.28	38	2.21	32	3.69		4.23	5.05	13.5	-15.06	106	45.4

(a) anomeric proton

(b) probably (A + B) = 4, C = 3 protons

(c) probably A = 1, B = 2, (C + D) = 4 protons

Table 56. 1,5-anhydro Mannitol

Conc. CoCl ₂ <u>M</u>	Peak A $\Delta\nu$ τ 1/2c/s	Peak B $\Delta\nu$ τ 1/2c/s	Peak C $\Delta\nu$ τ 1/2c/s	Peak D τ	Peak E τ	Peak F τ	OH $\Delta\nu$ τ 1/2c/s	Conc. D ₂ O <u>M</u>	
0	5.98	6.17	6.30	6.47		5.30		47.7	
1 ^a	3.66	20.1	4.26	19.7	5.19	12.0	5.4 5.62 5.98 -4.75	61	47.6
2 ^b	-1.09	70	0.67	34	3.66		4.30 5.05 6.08 -15.65	111	45.9

(a) A = 2, B = 1 proton.

(b) A = 2, B = 1 proton. Probably C = E = F = 1 proton, D = 2 protons.

Table 57. D-Galactose

Conc. CoCl ₂ <u>M</u>	Peak A $\Delta\nu$ τ 1/2c/s	Peak B τ	Peak C τ	Peak D τ	Peak E τ	Peak F τ		OH $\Delta\nu$ τ 1/2c/s	Conc. D ₂ O <u>M</u>
0	4.75 ^a	5.43 ^b	6.28 ^c					5.29	48.0
1	4.33	4.57	5.30	5.51				-4.75 63	46.8
2 ^d	1.11 45	2.25	2.86	3.41	3.98	4.28		-15.28 103	45.8

(a) α -anomeric:

(b) β -anomeric:

(c) main peak in spectrum; all other peaks within ± 0.25 . (d) A = 2 protons

Table 58. Methyl α -D-Galactopyranoside

Conc. CoCl ₂ <u>M</u>	Peak A $\Delta\nu$		Peak B $\Delta\nu$		Peak C $\Delta\nu$		Peak D $\Delta\nu$		OMe $\Delta\nu$		OH $\Delta\nu$		Conc. D ₂ O <u>M</u>
	τ	1/2c/s	τ	1/2c/s	τ	1/2c/s	τ	1/2c/s	τ	1/2c/s	τ	1/2c/s	
0	5.20 ^a		6.06		6.23				6.61	0.9	5.33	2.5	46.6
1	4.48	34	4.84	14.1	5.38	18			6.14		-4.88	64	46.1
2 ^b	1.30	45	2.36	27.4	3.67		4.34	18.9	5.45	14.9	-15.71	108	44.7

(a) anomeric proton.

(b) A = 2, B = C = 1, D = 3 protons.

Table 59. Methyl β -D-Galactopyranoside

Conc. CoCl ₂ \underline{M}	Peak A $\Delta\nu$ τ 1/2c/s		Peak B $\Delta\nu$ τ 1/2c/s		Peak C τ	Peak D τ	Peak E τ	OMe $\Delta\nu$ τ 1/2c/s		OH $\Delta\nu$ τ 1/2c/s		Conc. D ₂ O \underline{M}
0	5.69 ^a		6.07		6.25	6.43		6.43		5.28		-
1 ^b	4.32	16.7	4.98		5.33	5.55		5.88	8.1	-5.99	67	46.1
2 ^c	1.07	30.5	2.73	~19	3.6	4.0	4.3	4.97	18.9	-17.48	141	44.9

(a) anomeric proton.

(b) Probably A = 2 protons.

(c) Probably A = 2, B = 1 proton.

Table 60. 1,2-O-isopropylidene-D-glucofuranose

Conc. CoCl ₂ \underline{M}	Peak A $\Delta\nu$ τ 1/2c/s		Peak B $\Delta\nu$ τ 1/2c/s		Peak C $\Delta\nu$ τ 1/2c/s		Peak D $\Delta\nu$ τ 1/2c/s		Peak E $\Delta\nu$ τ 1/2c/s	
0	4.02 ^c	1.5	5.26	5.69	3.9	5.98	5.2	6.07	3.9	
1 ^e	3.41		3.68	4.74		5.04				
2	-2.94		-0.62	2.43		2.97		3.44		

Table 60 (Contd.)

Conc. CoCl ₂ \underline{M}	Peak F $\Delta\nu$ τ 1/2c/s		C·Me $\Delta\nu$ τ 1/2c/s		C·Me $\Delta\nu$ τ 1/2c/s		OH $\Delta\nu$ τ 1/2c/s		Conc. D ₂ O \underline{M}
0	6.29	3.9	8.49	2.1	8.65	2.1	5.36	2.3	45.1 ^a
1 ^e	3.41		7.74	7.6	7.95 ^d	6.9	-4.83	76	47.8 ^b
2	3.78		6.52		6.83 ^d		-15.77		47.4 ^b

(a) conc. acetone glucose 1M:

(b) conc. acetone glucose 0.25M:

(c) anomeric proton

(d) C·Me peak coincident with Me₄NCl peak

(e) Probably (A + B) = 4 protons, (C + D) = 3 protons.

Table 61. Ethyl-1-thio-D-glucufuranoside

Conc. CoCl ₂ M	Peak A		Peak B		Peak C		Peak D	
	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$
0 ^a	4.46 ^b	3.3	5.71		6.03		6.26	
1 ^e	2.7		3.15		3.73	8.2	4.62	
2 ^e	-4.3		-2.1		2.2		2.50	

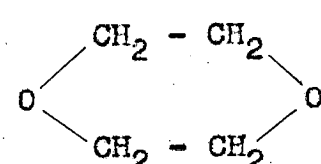
Table 61 (Contd.)

Conc. CoCl ₂ M	Peak E		Peak F		Peak G		OH		Conc. D ₂ O M
	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	
0 ^a	7.28 ^c	3.1	8.75 ^d	3.1			5.32	0.9	49.3
1 ^e	4.92	14.8	6.6 ^c		7.96 ^d		-4.62	71	-
2 ^e	3.32		3.55		5.43		-15.26		-

- (a) 0.5 M ethylthioglucofuranoside: (b) anomeric proton:
 (c) CH₂ of ethyl group: (d) CH₃ of ethyl group:
 (e) 0.25M ethylthioglucofuranoside.

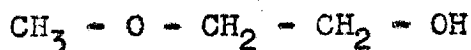
In order to facilitate discussion of the results and the correlation of contact shifts with structure the results are given below together with the molecular structure of the ligands. Where assignment of each peak in the spectrum is clear the results are presented as contact shifts in the negative field direction (i.e. in terms of $-\Delta\delta$ p.p.m.), but where no certain assignment of peak origin is possible the results are presented as τ values. In each case the results have been corrected to a tert-butanol (i.e. non shifted) reference by adding 0.8 p.p.m. and 2.0 p.p.m. to the τ values relative to the tetramethylammonium standard for 1M and 2M cobalt respectively (see section 3(V)). Thus a negative sign implies a positive, upfield shift.

In the results given below 1M and 2M refer to the molarities of the cobalt chloride in the solutions, and except where τ values are specifically labelled as such the shifts are given in p.p.m. from the corresponding diamagnetic resonance position.

Methanol (Table 1)		Ethanol (Table 2)		<u>n</u> -Propanol (Table 3)		
$\text{CH}_3 - \text{OH}$		$\text{CH}_3 - \text{CH}_2 - \text{OH}$		$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$		
<u>1M</u> :	3.6	<u>1M</u> :	0.4 2.1	<u>1M</u> :	0.0 0.2 1.6	
<u>2M</u> :	9.4	<u>2M</u> :	1.1 5.2	<u>2M</u> :	0.1 0.8 4.5	
<u>iso</u> -propanol (Table 4)		<u>n</u> -Butanol (Table 5)				
$(\text{CH}_3)_2 - \text{CH} - \text{OH}$		$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$				
<u>1M</u> :	0.2 0.5	<u>1M</u> :	0.0 -0.1 0.3 1.6			
<u>2M</u> :	0.5 1.4	<u>2M</u> :	0.0 -0.2 0.9 4.5			
<u>sec</u> -Butanol (Table 6)		<u>iso</u> -Butanol (Table 7)				
$\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_3$		$(\text{CH}_3)_2 - \text{CH} - \text{CH}_2 - \text{OH}$				
<u>1M</u> :	0.0 0.1 0.4 0.1	<u>1M</u> :	0.0 0.1 1.3			
<u>2M</u> :	0.0 0.4 1.2 0.3	<u>2M</u> :	0.1 0.3 3.7			
<u>tert</u> -Butanol (Table 8)		Acetone (Table 9)		Dioxan (Table 10)		
$(\text{CH}_3)_3 - \text{C} - \text{OH}$		$(\text{CH}_3)_2 - \text{CO}$				
<u>1M</u> :	0.1	<u>1M</u> :	-0.4	<u>1M</u> :	-0.3	
<u>2M</u> :	-0.1	<u>2M</u> :	-1.0	<u>2M</u> :	-0.4	

The small shifts apparently shown by tert-butanol, which is by definition unshifted after correction are a measure of the experimental error inherent in the correction method.

2-methoxyethanol (Table 11)



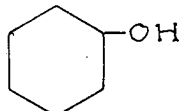
1M : -0.4 0.5 2.2
2M : -0.8 2.1 6.4

Digol (Table 12)



1M : 1.7 0.2
2M : 4.5 0.8

cyclohexanol (Table 13)



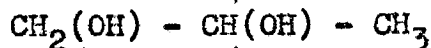
OM : A 8.3 τ ; B 8.7 τ
1M : A 5.2 τ ; B 7.5 τ ; C 7.9 τ
2M : A 3.2 τ ; B 6.6 τ ; C 6.6 τ

Ethylene Glycol (Table 14)



1M : 3.4
2M : 8.4

Propane-1,2-diol (Table 15)



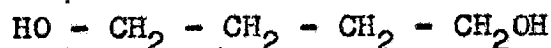
1M : A 5.6; B 2.7; C 1.4; CH₃ 0.6
2M : A 14.9; B 7.1; C 3.8; CH₃ 1.7

Propane-1,3-diol (Table 18)



1M : 4.0 0.1
2M : 10.3 0.4

Butane-1,4-diol (Table 20)

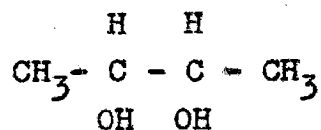


1M : 1.8 0.1
2M : 5.1 1.0

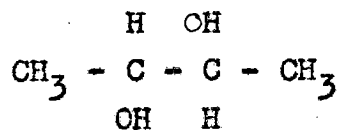
Butane-1,3-diol (Table 19)



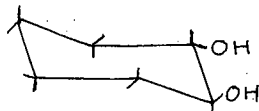
1M : A 4.8; B 2.8; C 1.9; CH₂ 0.2; CH₃ 0.5
2M : A 13.7; B 7.7; C 5.3; CH₂ 0.9; CH₃ 1.4 } A = B = C = 1H

meso-butane-2,3-diol (Table 21)

1M : CH 2.1; CH₃ 0.3
2M : CH 6.8; CH₃ 0.8

racemic-butane-2,3-diol (Table 22)

1M : CH 3.6; 2.8
2M : CH 9.3; 7.1

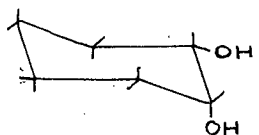
trans-cyclohexane-1,2-diol (Table 23)

OM : A 6.7τ; B 8.1τ; 8.4τ; D 8.8τ: - A = 2H

1M : A 4.7τ; B 6.9τ; 8.0τ; D 8.5τ

2M : A 1.6τ; B 4.6τ; 7.7τ; D 8.2τ

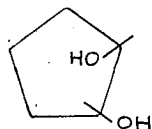
} A = B = 2H. Probably C = 2H, D = 4H.

cis-cyclohexane-1,2-diol (Table 24)

OM : A 6.2τ; B 8.5τ :- A = 2H

1M : A 2.2τ; B 7.6τ; C 8.6τ; D 8.6τ: - A = 2H

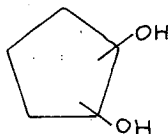
2M : A 4.8τ; B 6.1τ; C 8.8τ; D 9.6τ: - A = B = 2H; Probably C = 4H, D = 2H.

trans-cyclopentane-1,2-diol (Table 27)

OM : A 6.0τ; B 8.3τ :- A = 2H (CH-O)

1M : A 5.7τ; B 8.2τ

2M : A 5.1τ; B 7.8τ; C 8.2τ: - Probably A = B = 2H; C = 4H

cis-cyclopentane-1,2-diol (Table 28)

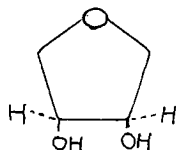
OM : A 6.0τ; B 8.3τ

:- A = 2H (CH-O-)

1M : A -2.8τ; B 6.8τ; C 8.1τ;

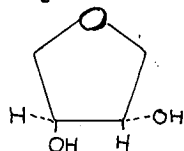
2M : A about -16τ; B 4.7τ; C 7.4τ; D 8.0τ;

1,4-anhydroerythritol (Table 29)



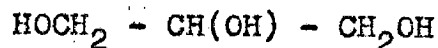
1M : CH 2.3; CH₂ 0.4, 0.0 CH₂ shifts referred to 6.2, i.e.
 2M : CH 6.8; CH₂ 1.4, 0.6 average of both resonances.

DL-1,4-anhydrothreitol (Table 30)



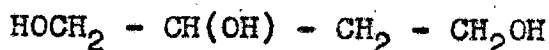
1M : CH 0.4; CH₂ 0.0
 2M : CH 0.9; CH₂ 0.3, -0.1.

Glycerol (Table 31)



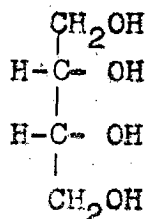
1M : CH 1.5; CH₂ 3.4, 2.5
 2M : CH 3.6; CH₂ 8.7, 6.5

Butane 1,2,4-triol (Table 32)



1M : A 3.9; B 2.6; C 2.2 ; CH₂ 0.7:-Probably A=B=2H; C=1H.
 2M : A 10.5; B 9.4; C 6.9; D 5.5; CH₂ 1.7:-Probably A=B=D=1H; C=2H.

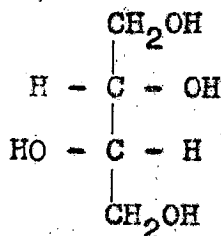
Erythritol (Table 33)



VI

1M : A 3.3; B 2.1; A=2H; B=4H
 2M : A 9.3; B 8.9; C 6.2; A=B=C=2H

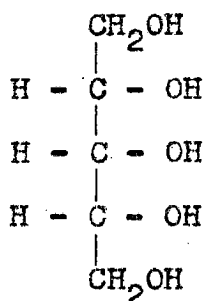
L-Threitol (Table 34)



VII

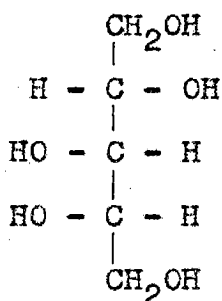
1M : A 3.3; B 2.9; C 2.2 } A = B
 2M : A 8.7; B 7.7; C 6.3 } = C = 2H

D-Ribitol (Table 35)



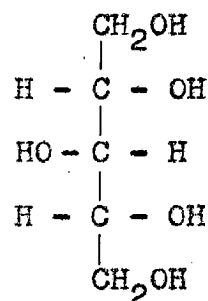
VIII

L-Arabitol (Table 37)



IX

Xylitol (Table 36)



X

D-Ribitol

$1\text{M} : \text{A } 4.0; \text{B } 2.8; \text{C } 2.1; \text{D } 1.5$
 $2\text{M} : \text{A } 10.4; \text{B } 7.7; \text{C } 6.5; \text{D } 4.2$

$\left. \begin{array}{l} 1\text{M} : \text{A } 4.0; \text{B } 2.8; \text{C } 2.1; \text{D } 1.5 \\ 2\text{M} : \text{A } 10.4; \text{B } 7.7; \text{C } 6.5; \text{D } 4.2 \end{array} \right\} \text{A} = \text{B} = \text{D} = 2\text{H}; \text{C} = 1\text{H}$

L-Arabitol

$1\text{M} : \text{A } 4.8; \text{B } 3.7; \text{C } 3.2; \text{D } 1.4; :- \text{D}=2\text{H}; \text{Probably } \text{A} = 1\text{H}, \text{B}=\text{C}=2\text{H}.$

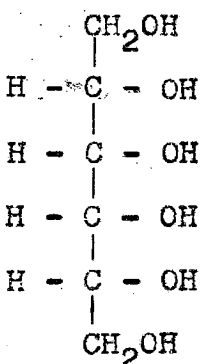
$2\text{M} : \text{A } 11.8; \text{B } 9.9; \text{C } 7.9; \text{D } 6.2; :- \text{Probably } \text{A} = 1\text{H}, \text{B} = \text{C} = \text{D} = 2\text{H}.$

Xylitol

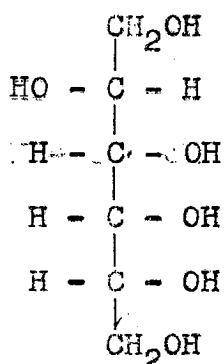
$1\text{M} : \text{A } 4.1; \text{B } 3.4.$

$2\text{M} : \text{A } 12.1; \text{B } 9.5; \text{C } 8.9; \text{D } 8.0$

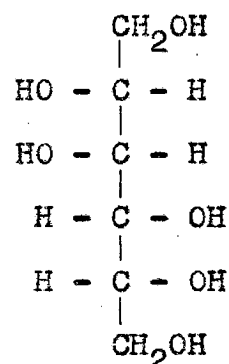
Allitol (Table 38)



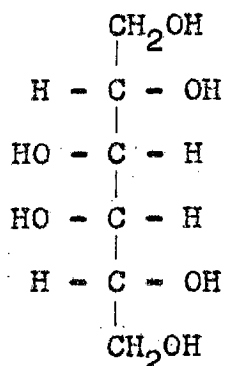
XI

D-Talitol (Table 43)

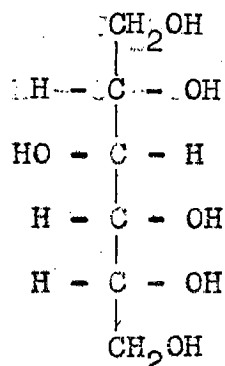
XII

D-Mannitol (Table 42)

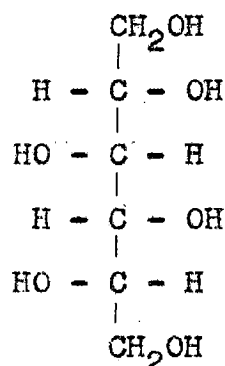
XIII

D-Dulcitol (Table 41)

XIV

D-Sorbitol (Table 39)

XV

L-Iditol

XVI

Allitol

$$\begin{array}{l}
 1\text{M} : \text{A } 5.3; \text{ B } 3.0; \text{ C } 1.6 \\
 2\text{M} : \text{A } 11.1; \text{ B } 7.6; \text{ C } 4.4
 \end{array}
 \left. \vphantom{\begin{array}{l} 1\text{M} \\ 2\text{M} \end{array}} \right\} \text{A} = \text{B} = 2\text{H}; \text{ C} = 4\text{H}$$

D-Talitol

$$\begin{array}{l}
 1\text{M} : \text{A } 5.7; \text{ B } 4.4; \text{ C } 3.8; \text{ D } 3.3; \text{ E } 2.3 \\
 2\text{M} : \text{A } 14.6; \text{ B } 11.5; \text{ C } 10.0; \text{ D } 8.8; \text{ E } 6.2
 \end{array}
 \left. \vphantom{\begin{array}{l} 1\text{M} \\ 2\text{M} \end{array}} \right\} \text{Probably } \text{A} = \text{B} = \text{E} = 1\text{H}$$

D-Mannitol

$$\begin{array}{l}
 1\text{M} : \text{A } 4.4; \text{ B } 3.5; \text{ C } 2.0 \\
 2\text{M} : \text{A } 11.8; \text{ B } 9.6; \text{ C } 5.7
 \end{array}$$

D-Dulcitol

$$\begin{array}{l}
 1\text{M} : \text{A } 3.7; \text{ B } 2.8 \\
 2\text{M} : \text{A } 9.9; \text{ B } 7.6
 \end{array}$$

D-Sorbitol

$$\begin{array}{l}
 1\text{M} : \text{A } 4.4; \text{ B } 3.3; \text{ C } 2.1 \\
 2\text{M} : \text{A } 11.3; \text{ B } 9.7; \text{ C } 6.9; - \text{C} = 2\text{H}; \text{ Probably } \text{A} = 2\text{H}, \text{ B} = 4\text{H}.
 \end{array}$$

L-Iditol

$$\begin{array}{l}
 1\text{M} : \text{A } 4.6; \text{ B } 3.4; \text{ C } 2.9 \\
 2\text{M} : \text{A } 13.1; \text{ B } 9.1; \text{ C } 8.0
 \end{array}
 \left. \vphantom{\begin{array}{l} 1\text{M} \\ 2\text{M} \end{array}} \right\} \text{A} = 2\text{H}; \text{ Probably } \text{B} = 2\text{H}; \text{ C} = 4\text{H}$$

(IV) Discussion

For all the ligands studied each solution containing cobalt gave only one set of resonances and so ligand exchange in the complexes must be sufficiently rapid to give complete averaging of the paramagnetic and diamagnetic environments. A full discussion of the mechanisms operative in the N.M.R. contact interactions is given later in section 3(IV)f. However for the purpose of the present discussion it may be noted that the magnitudes of the observed shifts will depend on two factors:

(a) the fraction of ligand present in the form of cobalt complexes and, (b) the nature of these complexes, i.e. the chemical shifts of the different protons in these complexes. Thus whether one ligand will give larger averaged contact shifts than another will depend both on the relative stabilities of the complexes and on the relative chemical shifts of protons within the two complexes. In interpreting the shifts obtained for various ligands these two points must be borne in mind and the possibility of both contact and pseudocontact shifts contributing to the observed shifts also taken into account.

As previously noted in the introduction to this section the ligands studied fall naturally into five groups; simple mono alcohols, simple diols, triols, polyols and carbohydrate derivatives, and the discussion of the ligand contact shifts obtained is grouped under these headings. Extension of the N.M.R. study of cobalt complexes to acids and hydroxy acids in aqueous solution and to alcohol ligands in non aqueous solution will also be discussed.

(a) Simple mono alcohols.

Considering the contact shifts obtained for the simple alcohols, two effects are immediately apparent; a chain length and a chain branching effect. Thus as the chain length increases in going from methanol to n-propanol and n-butanol the shifts obtained for corresponding positions decrease. It is interesting to note however that no real difference is shown in the shifts obtained for n-propanol and n-butanol, indicating that a limit exists for chain length, extension beyond which makes no difference to the shifts obtained.

Similarly, the greater the degree of branching and the closer the branching site to the alcoholic group the smaller the shift obtained. Thus whilst iso-butanol is only shifted a little less than n-butanol, iso-propanol and sec-butanol are shifted relatively much less than the corresponding normal alcohols, indicating the most important criterion is the degree of branching α - to the hydroxyl group. The order of shifts shown can thus be explained as being determined by the increasing degree of steric hindrance in the complex as the chain length and more especially the chain branching increases, all the more so if a high degree of free rotation is retained in the alcohol molecule when complexed.

However the relatively large shifts obtained for 2-methoxy ethanol at 2M cobalt are at variance with this explanation as it would be expected to show greater steric hindrance than ethanol and yet gives larger shifts, only methanol being shifted more. Consideration of the pK values⁹⁴ shows that methanol and 2-methoxy

ethanol have somewhat similar values whilst ethanol has a relatively much higher value as do the other primary alcohols. Since the greater the acidity, the lower the electron availability, consideration of pK values alone would indicate that ethanol would give rise to greater shifts than methanol and 2-methoxy ethanol even smaller shifts.

That methanol is shifted more than ethanol must then be due to greater steric hindrance in the ethanol complex. However 2-methoxy ethanol would still be expected to complex less than ethanol on both steric and electronic grounds considering the electron withdrawing nature of the methoxyl group.

When the contact shifts are corrected to tert-butanol as internal standard the methoxyl group in 2-methoxy ethanol then shows a small but definite upfield shift. In order to account for this assuming that complexing occurs only at the hydroxyl group, delocalisation as far as the ethereal oxygen followed by spin polarisation at the methyl group would have to be postulated. The occurrence of such a dual mechanism would seem to be unlikely specially as the shifts for the other alcohols when similarly corrected show that delocalisation only occurs as far as the β -CH₂ group (in agreement with Phillips, Looney and Ikeda³⁴).

If loose interaction between the etherial oxygen and the cobalt ion occurred however then spin density could possibly reach the oxygen atom more easily and a spin polarisation mechanism could then explain the upfield methyl shift. The same mechanism operating on the β -CH₂ group would then lead to a decrease in the

downfield shift produced by delocalisation from the hydroxyl group, and might thus explain the slightly larger α/β shift ratio in 2-methoxy ethanol than in ethanol.

A more probable explanation of the upfield methyl shift would be that if such a loose interaction between the etherial oxygen and the cobalt occurred, i.e. a form of chelation, then the close proximity of the methyl group to the cobalt ion would make pseudo-contact shifts relatively larger than if only hydroxyl interaction occurred. If such pseudocontact shifts were positive in sign, and if delocalisation of unpaired spin through the weak bond formed to the etherial oxygen was only marginal then the net result would be a small positive upfield shift for the methyl group. Such an interaction could also account for the observed upfield shift of dioxan. In any case such weak chelation would tend to increase the stability of the 2-methoxy ethanol complex and hence the degree of complexing and so explain the greater shifts obtained than for ethanol. That no upfield shifts are shown for digol is not surprising as complex formation can occur through a hydroxyl group at both ends, and so the β -CH₂ would thus correspond to that in 2-methoxy ethanol which also gives a downfield shift. That the actual shifts for digol are smaller is then due to the greater steric hindrance arising from the greater chain length.

(b) Simple diols

In the following discussion of the shifts obtained for polyhydroxy alcohols and carbohydrate derivatives, for ease of reference and simplicity of discussion the peaks will be referred to as

peak A, B etc., with the convention that A refers to the most shifted peak, B to the next most shifted peak and so on. Where the origin of a peak is certain, as for the methyl group in the butane 2,3 diols they will be named according to origin. Further, unless otherwise stated the spectra referred to are those for solutions containing 2M cobalt since resolution into individual peaks is better at this concentration, and, except for the pyranose and furanose derivatives the shifts discussed are those corrected to a tert-butanol (1.e. non shifted) reference.

The large shifts obtained for the 1,2 and 1,3 diols indicate that chelation rather than mono-site complexing occurs as does the inequivalence of the protons on the 1-carbon atom shown by propane-1,2-, and butane-1,3-diol.

That 1,3 chelate formation occurs is rather surprising in view of the inherent instability of a six membered ring relative to a five membered ring⁹² and the report that propane-1,3-diol does not form a complex with cuprammonium⁹³. However the shifts obtained cannot be explained by only mono complexing occurring as the shifts in propane-1,3-diol should then be similar to those in methanol and n-propanol whereas the α -CH₂ shift is much larger and the β -shift much smaller. Mono complexing should in fact lead to a somewhat larger β -CH₂ shift than in ethanol or propanol as the central CH₂ is effectively β -twice, since complexing could occur at either end. The close similarity between the shifts of butane-1, 4-diol and ethanol indicates that as expected only end monodentate complexing occurs.

The inequivalence of the protons in propane-1,2-diol is very interesting as it shows the dependence of electron spin transfer on dihedral angle. Whilst pseudocontact effects might be expected to be different for various protons in the molecule the difference in shift of 10 p.p.m. between peaks A and C is too large to be due solely to pseudocontact shifts, especially as the shift of peak A is only 15 p.p.m, and so must be mainly due to differences in contact shifts. The assignment of the peaks in the propane-1,2-diol spectrum can be obtained by comparison of the shift ratios in propane-1,2-diol with those of 2-C-deutero propane-1,2-diol. For the corrected shifts these ratios are:

Diol	Conc. CoCl ₂	B/A	C/A	CH ₃ /A
Propane-1,2-diol	1M	0.48	0.25	0.11
	2M	0.48	0.26	0.11
2-C-deuteropropane-1,2-diol	1M	0.48		0.12
	2M	0.47		0.12

Thus the CH proton on C2 can be assigned to peak C, the least shifted of the single proton peaks. This assignment has been checked by addition of propane-1,2-diol to the 2-C-deutero propane-1,2-diol solution containing 1M cobalt whence a new peak of smaller intensity appeared to high field of the two single peaks previously obtained. Thus the two most shifted peaks A and B arise from the CH₂OH group.

The most stable form of the cobalt-propane-1,2-diol complex would be expected to be that in which the methyl group is equatorial

to the five membered chelate ring, in which case the CH proton on C2 would be axial, and one of the two protons on C1 also axial, the other equatorial to the chelate ring. Thus in the chelate there are two axial protons and only one equatorial proton which is hence unique and must correspond to either peak A or peak B. Since the two least shifted peaks B and C are coincident at low cobalt concentrations and only move apart slowly as the cobalt concentration is increased, and since of these peak C is due to the axial proton on C2 then peak B must correspond to the axial proton on C1. Thus the most shifted peak (A) must be due to the unique equatorial proton on C1. A large difference in contact shift is thus shown by protons axial and equatorial to a five membered chelate ring on the same carbon atom, the difference in the averaged shifts in the case of propane-1,2-diol being about 8 p.p.m. at 2M cobalt.

The difference in shifts obtained for the two axial protons (peaks B and C) must then be due to the effect of the equatorial methyl group in the chelate at C2 leading to a smaller shift for the axial proton at the same carbon atom. In propane-1,2-diol this effect leads to a difference in averaged shifts of more than 3 p.p.m. at 2M cobalt. An example of the spectrum of propane-1,2-diol in the presence of 2M cobalt is given in figure 1.

These differences in contact shifts due to differing orientation to the chelate ring and substitution effects could be used to distinguish between different substituents on an α -diol, for example to determine the stereospecificity of deuteration of

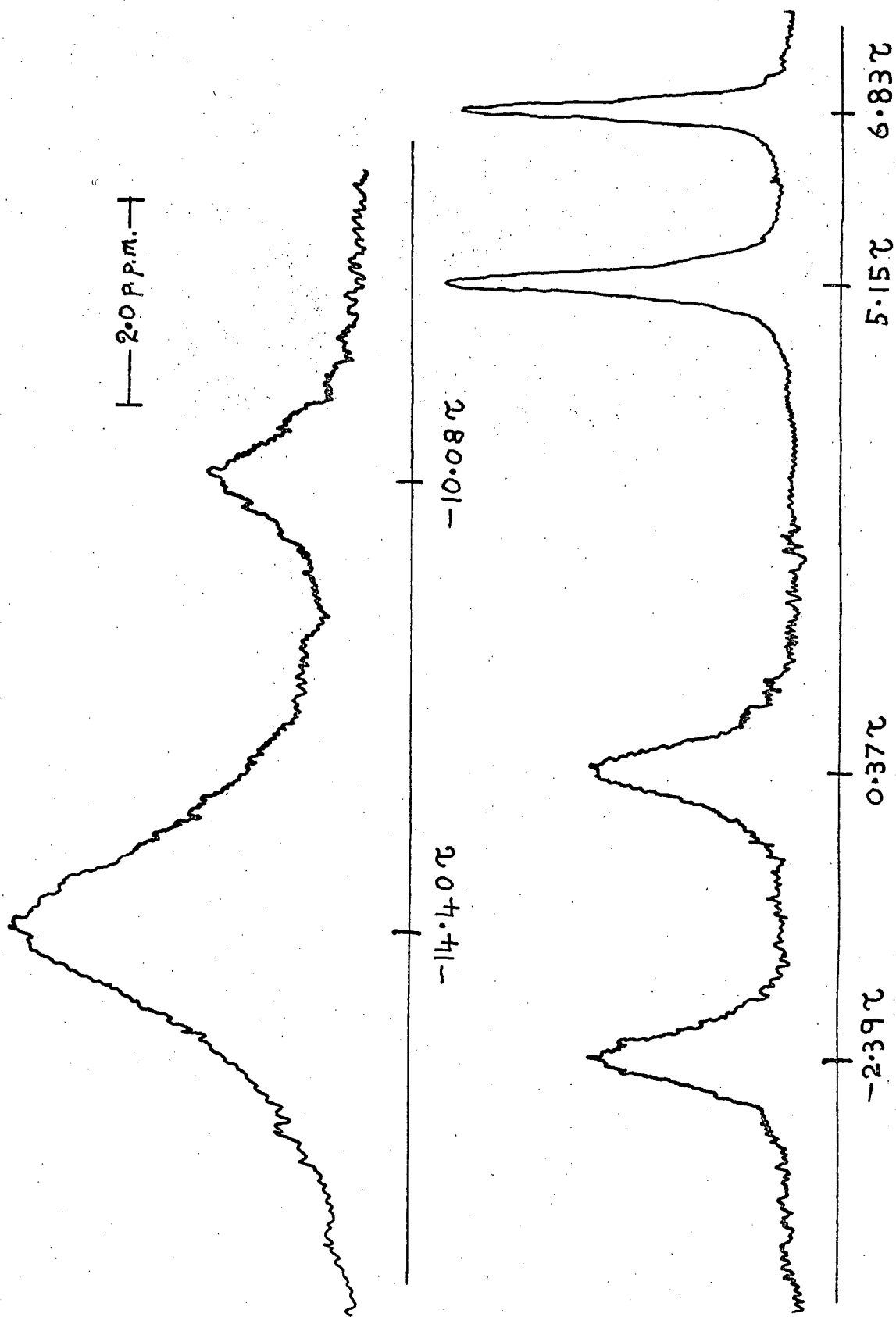


Fig. 1. 1M propane-1,2-diol + 2M cobalt(II)
(internal standard tetramethylammonium as 6.83)

say $R-CH(OH)-CHO$.

The qualitatively similar distribution of the shifts of peaks A, B and C in butane-1,3-diol to those in propane-1,2-diol tends to indicate that a similar dependence of spin transfer on dihedral angle occurs in a six membered chelate ring to that in a five membered ring. The most stable conformation of the chelate ring in butane-1,3-diol would be expected to be that in which the methyl group is equatorial to the ring at C3. In this conformation there would thus be two protons axial to the chelate ring at a carbon-oxygen junction and one equatorial. Thus peak A may be assigned to the equatorial proton on C1, peak B to the axial proton at C1 and peak C to the axial proton at C3. The difference in shift between the two axial protons again may be ascribed to the effect of the equatorial methyl substituent at C3 as in propane-1,2-diol. That the methyl group is shifted slightly more than the CH_2 group at C2 is also very interesting in that it indicates a preferred electron spin transfer from the oxygen when the Co-O and C-C bonds are "trans" than when they are gauche. The greater shifts of the equatorial proton at C1 as compared with the axial proton in both propane-1,2- and butane-1,3-diol are due to this preference for a trans orientation to the Co-O bond. This greater electron spin coupling in a trans orientation is analogous to the greater trans coupling constant than cis coupling constant in ethylenes. The equivalence of the two protons of the CH_2 group at C2 implies that no such great dependence of spin transfer on dihedral angle exists for the position between the complexing sites.

That the average shift of the two most shifted peaks in butane-1,3-diol is greater than the conformationally averaged shift of propane-1,3-diol indicates that the former probably complexes to a greater extent than the latter. The same behavior is shown by propane-1,2-diol relative to ethylene glycol, the compound with a methyl substituent complexing more than the unsubstituted compound. This behaviour is consistent with the order of the stability constants of the corresponding di-amines complexed with Ni(II) ⁷².

Comparison of the two isomeric diol pairs meso- and racemic-butane-2,3-diol and trans- and cis-cyclohexane-1,2-diol indicate the same preferred electron spin transfer through an O-CH-CH_n arrangement when the C-C and Co-O bond are trans to each other as was found for the methyl group in butane-1,3-diol. However the relationship between the proton shifts at the carbon-oxygen linkage are rather disconcertedly inverted in the two pairs.

In the most stable form of the racemic-butane-2,3-diol chelate both methyl groups will be equatorial to the chelate ring whereas in the meso complex one must of necessity be axial, and so the racemic complex will be much more stable. In the racemic complex both C-H protons will be axial and in the meso complex one will be axial the other equatorial, and so the C-H protons in the latter complex would be expected to be shifted more than in the racemic complex. That the C-H proton shift is greater for the racemic diol than for the meso diol can thus only be due to a greater degree of complexing occurring with the racemic diol.

However the greater relative shift of the methyl group compared with the C-H proton shift in the racemic diol than in the meso diol cannot be explained by a greater degree of complexing of the racemic diol, and must be due to their equatorial orientation in the racemic complex. Thus a relationship between axial and equatorial methyl groups must exist similar to that between axial and equatorial hydrogens found in propane-1,2-diol, an equatorial methyl group similarly being shifted more than the corresponding axial methyl group.

A dependence of electron spin coupling on dihedral angle however cannot explain the very small shift of the methyl group in meso-butane-2,3-diol since the shift will be the average of an axial and an equatorial methyl shift. Thus a positive pseudo-contact shift must be experienced by the axial methyl group of such a magnitude as to almost cancel the negative contact shifts experienced by both methyl groups, and especially the equatorial one. Thus both dihedral angle and pseudocontact effects must be important with bulky substituents axial to a chelate ring in which the protons are relatively close to the cobalt ion.

Considering the complexes formed by the cyclohexane-1,2-diols, the protons at the complexing sites will both be axial to the chelate ring in the trans-diol complex and one axial, one equatorial in the cis-diol complex. On the basis of the structure of the complexes it would thus be expected that the greatest shift would be shown by the cis-diol as was found in practice. However this argument neglects the difference in the extent of complexing of the

two diols. The stability constants of the cobalt complexes of the cis- and trans-cyclohexane-1,2-diamines and of the meso- and racemic-butane-1,2-diamines^{72,95} suggest that these differences would be similar for the butane-1,2-diols and the cyclohexane-1,2-diols. By analogy with the butane-2,3-diols it might thus be expected that trans-cyclohexane-1,2-diol would show the greater shift whereas in practice the cis diol gives the larger shift. However any conclusions about the relative complexing strengths of these diols drawn from the stability constants of the corresponding diamine complexes must be treated with great reservation. Whilst the stability constant of the Ni(II) complex with propane-1,2,3-triamine⁷² is greater than those of the butane and cyclohexane diamine complexes, glycerol, as is shown later, does not appear to form a tridentate 1,2,3 cobalt complex, and indeed gives smaller shifts than any of the butane or cyclohexane diols.

The peaks in the trans-cyclohexane-1,2-diol spectrum may be fairly unambiguously assigned by consideration of the structure of the complex. In this case only one stable conformation of the cyclohexane ring exists, namely that in which both hydroxyl groups are equatorial to the cyclohexane ring, and so only one complex conformation is possible. The most shifted peak, of intensity two (peak A) may then be assigned to the protons on C1 and C2. Peaks B and C, both also of intensity two may then be assigned to the protons axial on C3 and C6 and equatorial on C3 and C6, although the precise assignment as to which is which cannot be made with certainty. By analogy with the greater shift of an equatorial

substituent than an axial one found in propane-1,2-diol and the butane-1,2-diols it might be expected that the equatorial protons on C3 and C6 would be shifted more than the axial protons, and if so, the equatorial protons may be assigned to peak B and the axial to peak C. Peak D, of intensity four thus arises from the protons on C4 and C5.

In cis-cyclohexane-1,2-diol however, the peak assignments are much more obscure, although that peak D shows a definite upfield shift, and peak C perhaps a marginal one clearly indicates that pseudocontact shifts are of importance in this system. Following the assignment in the trans diol, and ascribing peak A (intensity two) to the protons on C1 and C2, and the intensity four peak (C) to the protons on C4 and C5, then of the protons on C3 and C6 two are shifted downfield and two upfield. These protons are equivalent in pairs, one proton on each carbon, depending whether they are cis- or trans- to the hydroxyl group on the neighbouring carbon atom.

Comparing molecular models of the two cyclohexane-1,2-diol complexes it can be seen that in any one of the two possible cis diol complex conformations one cyclohexane ring junction is axial to the chelate ring, the other equatorial, whereas in the trans diol complex both are equatorial. Considering the cis diol conformation in which the hydroxyl groups are equatorial on C1 and axial on C2 with respect to the cyclohexane ring then in the complex C6 is axial and C3 equatorial to the chelate ring. By analogy with the very small axial methyl shift in meso-butane-2,

3-diol the protons on C6 would be expected to show very little downfield shift, and may in fact show an upfield shift. The proton on C6 cis to the hydroxyl group on C1 (to which the proton on C3 cis to the hydroxyl group on C2 is conformationally equivalent) is then pointing towards the cobalt atom, while the other proton on C6 is pointing away. The other pair of equivalent protons, those trans to the hydroxyl groups, are relatively further away from the cobalt ion but still closer than any proton on C3 or C6 in the trans diol complex.

Thus the shifts for both pairs of equivalent protons on C3 and C6 in the cis-diol complex will be the average of those from two different environments; in one of which fairly large downfield shifts will be experienced, the other in which very small downfield shifts or even fairly large upfield pseudocontact shifts will be experienced. In view of the great dependence of pseudocontact shifts on distance from the central ion it is plausible to assume that the greater pseudocontact shift will be experienced by those protons closest to the cobalt ion in both possible conformations. Thus peak D may be tentatively assigned to the protons on C3 and C6 cis to the hydroxyl groups on C2 and C1 respectively, and peak B to those protons trans to the corresponding hydroxyl groups. Unambiguous assignment of all the protons in the molecule would require selective replacement of the protons on C3 and C6 preferably by deuterium or possibly even by fluorine which is small enough not to produce any preferred conformation.

With the cyclopentane diols and the corresponding 1,4-anhydro

tetritols the interpretation of the shifts and their relative magnitudes is comparatively straightforward. That trans-cyclopentane-1,2-diol shows virtually no shifts can be easily understood on consideration of a molecular model which shows that the complex would be very highly strained, and hence chelate formation is extremely unlikely. Such small shifts that are shown most probably arise from monocomplexing although even here there will be fairly large steric hindrance. Similar considerations apply to 1,4-anhydrothreitol in which chelate formation would also give rise to a very highly strained system and so is unlikely to occur. Another factor operative in 1,4-anhydrothreitol which would tend to reduce complexing is the electron withdrawing nature of the ring oxygen which would tend to reduce electron availability at the hydroxyl groups. The small shifts obtained must then be due to a little mono complexing occurring.

With the corresponding cis-diols however chelation would give a complex in which the ring systems are mobile and relatively free from ring strain. Examination of molecular models shows that in the complex both the cyclic diol and the chelate rings are very mobile and hence the precise conformation adopted in the complexes cannot be predicted with certainty. However in order to avoid eclipse interactions the chelate ring will tend to exist in a puckered ring form and the cyclopentane or 1,4-anhydro ring to exist in an "envelope" conformation. The very large shifts for the CH group protons in cis-cyclopentane-1,2-diol can then be explained by the ease of complex formation and the consequent relatively large fraction

complexed. Electron withdrawal by the ring oxygen and consequent decrease in the tendency to complex in 1,4-anhydroerythritol would lead to smaller shifts as observed in practice.

In the cis-cyclopentane-1,2-diol spectrum peak A may be unambiguously assigned to the two protons on C1 and C2, but the remaining peaks can only be tentatively assigned by analogy with other diols. In the complex the protons on C3 and C5 cis to the hydroxyl groups will always be closer to the cobalt ion, and those trans to the hydroxyl groups might be expected to experience the greater electron spin transfer in view of the previously noted preference for larger coupling over large dihedral angles. Thus peak B may be assigned to the protons on adjacent carbon atoms trans to the hydroxyl groups, peak C to the corresponding cis protons and peak D to the two protons on C4. The assignment of the peaks in the 1,4-anhydroerythritol will then be exactly the same as for peaks A, B and C in cis-cyclopentane-1,2-diol.

The great differences in the patterns of shifts shown by isomeric 1,2-diols renders possible the determination of fraction of each isomer in a mixture of both. Examples of this are shown in Tables 25 and 26 for the butane-2,3-diols and the cyclohexane-1,2-diols. The peaks shown in the spectra of the mixtures can easily be assigned by reference to the spectra of the individual diols (Tables 21 to 24 inclusive). The relative mole fractions of the two isomers in the mixture can then be simply determined by comparing the relative intensities of corresponding peaks from the two isomers.

(c) Simple Triols

Whereas with diols only one chelate ring can be formed, with triols there exists the possibility that more than one type of chelate ring may be formed. Considering glycerol, 1,2 chelation (which is equivalent to 2,3 chelation), 1,3 chelation or even 1,2,3 chelation are in principle possible.

Considering 1,2,3 tridentate chelation then two five membered rings would be formed with one proton on C1 axial the other equatorial to the 1-2 chelate ring, and one axial and one equatorial proton to the 2-3 chelate ring at C3. The CH proton at C2 would be equatorial to both chelate rings. It would thus be expected that three protons would be shifted more than the remaining two axial protons which would themselves be equivalent. That peaks A and B are both of intensity two and the least shifted peak (C) of unit intensity would thus rule out tridentate chelation. In agreement with this is the observation by Bourne et al.⁹⁶ that in electrophoresis in molybdate electrolyte solution glycerol does not migrate, although certain cyclic cis, cis triols do form tridentate complexes in this system.

If bidentate 1,3 chelation occurs then the most probable chelate conformation would be a chair form of the six membered ring in which the hydroxyl group at C2 is equatorial. Thus there will be one axial and one equatorial proton on both C1 and C3, and hence the spectrum would be two peaks of intensity two and a peak of intensity one less shifted. Thus 1,3 chelation could give rise to the observed order of peak intensities. However, that peak A in glycerol is shifted much less than those for propane-1,3-diol

and butane-1,3-diol whilst peak C is shifted much more than the CH_2 protons situated between the complexing sites in the 1,3-diols indicates that 1,3 complexing in glycerol is relatively unimportant.

In a bidentate 1,2 chelate the situation would be the same as in propane-1,2-diol in that one proton of the CH_2OH group would be axial to the chelate ring and the other equatorial, with the proton on C2 axial and the remaining hydroxy-methyl group equatorial to the chelate ring. The distribution of the shifts in the complex would then be similar to those in propane-1,2-diol. Since 2,3 chelation is equivalent to 1,2 chelation the peaks would thus be in three groups; the axial protons on the CH_2 groups, the equatorial protons and the CH proton. The shifts of the CH_2 protons will be averaged and the resulting shifts, in order of decreasing shift would thus be; (A), the average of an equatorial proton and an equatorial hydroxy-methyl shift, (B), the average of an axial proton and an equatorial hydroxymethyl shift, both of intensity two, and (C), an axial proton on the same carbon atom as an equatorial substituent. Thus compared with propane-1,2-diol the shifts of peaks A and B would be less and that of the CH proton similar to those in propane-1,2-diol, the net result being a less spread out spectrum as is observed. The predominant form of complex formation with glycerol is thus vicinal bidentate chelation.

With butane-1,2,4-triol if bidentate 1,2 chelation occurs then the distribution of the shifts for the protons on C1 and C2 would be similar to those in propane-1,2-diol. The protons on C3 would be shifted less and those on C4 even less still. Thus the

intensities of the peaks in order of decreasing shift would be expected to be one, one, one, two and two. That peak C is of intensity two would thus rule out exclusive 1,2 chelation. If simultaneous mono complexing at C₄ as well as 1,2 chelation were to occur then the protons on C₄ would experience an additional fairly substantial shift and the protons on C₃ would be shifted by the sum of an equatorial group on a five membered chelate ring and that of a β -group in a mono alcohol. The two CH₂ groups at C₃ and C₄ would then be expected to show rather similar shifts. That of the two intensity two peaks C and E one shows a large shift and the other a small shift would thus tend to negate bidentate 1,2 chelation.

If tridentate chelation occurs then a fused five and six membered chelate ring system will be formed. At C₁ there then would be one proton axial and one equatorial to the five membered chelate ring and one equatorial to both chelate rings at C₂ with a ring residue axial at that position. Thus a propane-1,2-diol type of distribution of contact shifts with the proton at C₂ least shifted would be expected. The most favoured conformation of the six membered ring would be expected to be a chair conformation and so there would be an axial and an equatorial proton at C₄; the axial one is pointing towards the cobalt ion and so might be expected to be shifted less due to pseudocontact effects.

The observed pattern of contact shifts and peak intensities may then be rationalised in terms of orientation to the chelate ring, substituent and pseudocontact effects as for the various open

chain and cyclic diols. Peak A (intensity one) may be assigned to the equatorial proton at C1, peak B (intensity one) to the equatorial proton at C4 and peak D, the remaining intensity one peak to either the axial proton at C1 or the axial proton at C4. Peak C, the first two proton peak, would then arise from the equatorial proton at C2 and either the axial proton at C4 or that at C1. If pseudocontact effects are important for the axial proton at C4, which is closest to the cobalt ion, then this might be expected to be shifted less than the corresponding axial proton on C1 and hence the latter would then contribute to peak C and the former would give rise to peak E. The remaining peak of intensity two, peak D would then be due to the protons at C3 thus completing the assignment.

Absolute assignment of the peaks in the spectrum would require in turn selective deuteration of both protons at C4 and that at C2. However in butane 1,2,4 triol it is clear that the dominant complex is a tridentate complex.

(d) The Polyols.

Whereas the spectra of the simple diols and triols can be easily explained in terms of molecular structure, and, in most cases, a fairly unambiguous assignment of peaks in the spectra to the various protons in the molecules made, in the polyols the situation is more obscure. Considering only 1,2, and 1,2,4 type chelation, the possible number of complexes which could be formed is very high, especially for the hexitols, although some may be discounted in view of the instability of a chelate ring if bulky axial substituents

are present or if substituents interact with each other. Even so there still remains a fairly high number of possible complexes which could be formed.

One thing is certain however, and that is that stronger complexing occurs with the polyols than say with the diols as not only do the most shifted peaks exhibit large shifts but so too do the least shifted peaks, especially in the hexitols.

The hexitols are also very interesting in that with the exception of talitol which has five, and dulcitol which has two, they all give only three peaks, indicating that despite great differences in configuration the types of complexes occurring with each one must have some protons in rather similar environments. The pentitols however give more peaks but the tetritols in view of the symmetry of the molecule give as expected fewer peaks.

Considering the two tetritols, erythritol (VI) and threitol (VII), the two most shifted peaks exhibit greater shifts in the case of erythritol than of threitol, whereas the least shifted peak is shifted the same in both.

If only vicinal end complexing occurs with both ligands then the most stable chelate conformation will be the same in both cases; that in which the rest of the polyol chain is equatorial to the chelate ring. By symmetry 1,2 and 3,4 complexing will be equivalent. In the chelate there will be one proton axial and one equatorial to the chelate ring at C1 (or C4) and an axial proton at C2 (or C3) with the rest of the chain equatorial at that position. In this case both tetritols should give rise to very similar spectra showing very nearly identical distribution of shifts since the only

difference between the two chelates would be the different conformations adopted by the side chain to the chelate ring necessary by virtue of their different configuration. That in fact the shift ratios are rather markedly different, with erythritol showing a smaller separation between the two most shifted peaks than does threitol would thus tend to cast doubt on exclusive end chelation. End chelation can also be definitely ruled out by comparison of the magnitude of the shifts in the tetritys with those in propane-1, 2-diol, especially those of peak C in each spectrum. While the chelate type is the same in all three ligands the shift of the proton at C2 in propane-1,2-diol is exclusively that of a proton axial to the chelate ring on a carbon carrying an equatorial substituent. The corresponding proton in the tetritys is averaged with that of the actual substituent. That both the peak C shift and the substituent shift in propane-1,2-diol are much less than the peak C shifts in the tetritys thus rules out end complexing in the tetritys, especially when it is considered that the actual degree of complexing will be less than for propane-1,2-diol due both to the greater steric hindrance and lower electron availability in the polyols.

If only 2,3 chelation were to occur then erythritol should give shifts analogous to those of meso-butane-2,3-diol, and threitol analogous to those shown by racemic-butane-2,3-diol which they manifestly do not as erythritol gives the greater shifts. Further, such chelation should only give rise to two peaks of intensities two and four respectively, unless preferred orientation of the hydroxyl

group in the hydroxymethyl substituents occurs. Thus exclusive 2,3 chelation must also be ruled out.

The only possible exclusive form of chelation remaining is thus 1,2,4 and 1,3,4 tridentate chelation. In 1,2,4 (1,3,4) chelation erythritol would have the remaining hydroxyl group at C3 (C2) axial to the six membered chair chelate ring whereas with threitol it would be equatorial in the most stable chair conformation. Thus the threitol complex would be expected to be more stable than the erythritol chelate.

In the case of threitol the proton of C1 which is axial to the five membered chelate ring in the 1,2,4 chelate is also axial to the six membered ring in the 1,3,4 chelate. With erythritol however the proton at C1 axial to the five membered ring in the 1,2,4 chelate becomes equatorial to the six membered ring in the 1,3,4 chelate. Thus peaks A and B in the threitol spectrum would be due to the protons always equatorial and axial respectively whereas in the case of erythritol axial-equatorial averaging would occur in both cases. If the shifts of a proton in a five membered ring and in the same orientation in a six membered chelate ring are different, as is indicated by the shifts in the butane-1,2,4-triol spectrum, then since averaging occurs the separation between the two most shifted peaks in erythritol would be expected to be smaller than those in threitol as is the case in practice. The close identity of the least shifted peaks in both ligands can be easily understood as with both it would be due to the protons on C2 and C3 which are in virtually the same environment in both tetritol chelates. The shift

would represent the average of that for a proton equatorial to both rings at the junction of the chelate rings and that of a proton situated between the complexing sites in a six membered chelate ring. The results obtained for butane-1,2,4-triol indicate that in the latter situation orientation to the chelate ring at that point makes little difference, if any, and that only a small shift is experienced by protons in such an environment. Hence the shifts for peak C in both tetritols would be very similar, as is found in practice.

However, as threitol would give protons always in an equatorial orientation to the chelate rings it would be expected that it would give the greater shift for peak A, especially as the chelate formed would be more stable, it having the remaining hydroxyl group equatorial to the six membered ring unlike erythritol. In fact the larger shift is given by erythritol.

Thus while 1,2,4 and 1,3,4 tridentate chelation would explain satisfactorily the observed pattern of shifts it cannot explain their relative magnitudes. The conclusion must then be that while tridentate chelation probably occurs, and is probably the dominant chelate form, other chelate types are probably also formed to differing extents with threitol and erythritol.

Considering the pentitols and hexitols the number of possible complexes increases rapidly as the chain length increases. For example, the pentitols could in principle form four bidentate 1,2 type complexes and three 1,2,4 tridentate types whereas for the hexitols the numbers are five and six respectively. Detailed consideration of all the possible complexes which could be formed for

each ligand in turn and averaging of the environments of each proton in turn is a prohibitive exercise, especially for the hexitols, not only because of the total number of possible complexes but also because of the few peaks actually shown in the spectra.

However for ribitol at least, one peak in the spectrum can be unambiguously assigned. No matter what complex is actually formed the proton at position three in the chain is unique, and hence the only single proton peak in the spectrum (the third most shifted peak) must be due to this proton.

Although consideration and comparison of the various contact shifts observed for the polyols yields no real correlation of shift with structure, (except perhaps that in the pentitols at least, the greater the number of trans hydroxyl groups the greater the shift of the most shifted peak), comparison of the shift ratios within each individual spectrum shows that the polyols may be divided into three groups. If the ratios of the corrected shifts are calculated, with the most shifted peak in each case arbitrarily set as unity, then the following results are obtained.

Table 62.

Polyol	Cobalt conc.	Shift Ratios
Erythritol	1M	1.00 : 0.64
	2M	1.00 : 0.96 : 0.67
Threitol	1M	1.00 : 0.88 : 0.67
	2M	1.00 : 0.89 : 0.72
Ribitol	1M	1.00 : 0.70 : 0.53 : 0.38
	2M	1.00 : 0.74 : 0.63 : 0.40

(Contd.p.102)

Table 62 (Contd.)

Polyol	Cobalt conc.	Shift Ratios
Arabitol	<u>1M</u>	1.00 : 0.77 : 0.67 : 0.29
	<u>2M</u>	1.00 : 0.84 : 0.67 : 0.53
Xylitol	<u>1M</u>	1.00 : 0.83
	<u>2M</u>	1.00 : 0.79 : 0.74 : 0.66
Allitol	<u>1M</u>	1.00 : 0.57 : 0.30
	<u>2M</u>	1.00 : 0.69 : 0.40
Talitol	<u>1M</u>	1.00 : 0.77 : 0.67 : 0.58 : 0.40
	<u>2M</u>	1.00 : 0.79 : 0.69 : 0.60 : 0.42
Mannitol	<u>1M</u>	1.00 : 0.80 : 0.45
	<u>2M</u>	1.00 : 0.81 : 0.48
Dulcitol	<u>1M</u>	1.00 : 0.76
	<u>2M</u>	1.00 : 0.77
Sorbitol	<u>1M</u>	1.00 : 0.75 : 0.48
	<u>2M</u>	1.00 : 0.86 : 0.61
Iditol	<u>1M</u>	1.00 : 0.74 : 0.63
	<u>2M</u>	1.00 : 0.70 : 0.61

Comparing the shift ratios at 1M and 2M cobalt three groups can be distinguished. Xylitol (group 1) shows a decrease in shift ratio in going from 1M to 2M cobalt; talitol, mannitol, dulcitol, iditol and threitol (group 2) show virtually no change in shift ratios on changing the cobalt concentration, and erythritol, arabitol, ribitol, allitol and sorbitol (group 3) show an increase in shift ratios on changing from 1M to 2M cobalt.

That the polyols in group two show no change in shift ratios would indicate that the complexes formed by these ligands are probably specific and well defined, whereas that the polyols in the other groups do show changes in their shift ratios indicates that

the types of complexes formed, or at least their relative proportions, change as the cobalt concentration changes.

The composition of group two is interesting in that with the obvious exception of threitol these polyols are the only ones that can form tetradentate complexes; iditol a 1,3,4,6 complex, talitol a 1,2,4,6 complex, dulcitol both a 1,2,4,6 and a 1,3,5,6 complex and mannitol all three. Sorbitol (group 3) however would also form both a 1,3,5,6 and a 1,2,4,6 complex. Formation of such a tetradentate complex would effectively fix the ligand and so no other complex could be formed by the same molecule. It may be that such a type of complex formation where no other complex is formed could account for the constant shift ratios of these ligands, although that sorbitol does in fact show a change in shift ratios tends to indicate that any such specific complex formation is not of the tetradentate type.

The composition of the three groups cannot however be explained solely in terms of the configurational patterns within the polyols comprising each group as some configurational arrangements are common to polyols in different groups.

Thus in order to interpret the shifts and the shift patterns selective replacement studies would be necessary, either by selective methylation of the different hydroxyl groups or by selective replacement of hydrogen by deuterium, or preferably a combination of both.

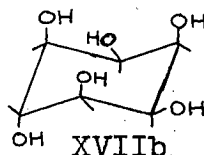
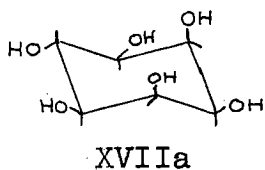
While a complete analysis of the type of complex formation occurring with erythritol and threitol has not been possible it is interesting to note that as tridentate chelation appears to be the

dominant type of chelation they thus appear to be more closely akin to butane-1,2,4-triol than to glycerol in their behaviour towards cobalt.

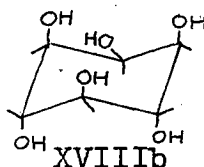
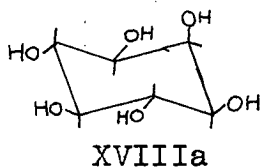
(e) Inositols, furanose and pyranose derivatives

In order to facilitate the discussion in this section the structure of the compounds under discussion are given below. Where appropriate alternative conformations are given.

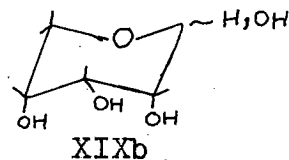
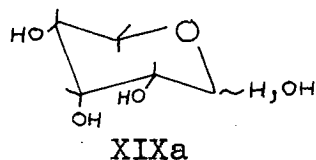
epi-inositol



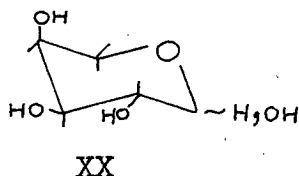
myo-inositol



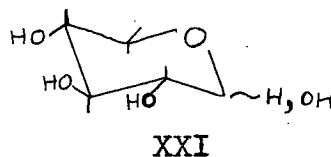
D-ribopyranose



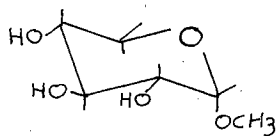
L-arabinopyranose



D-xylopyranose

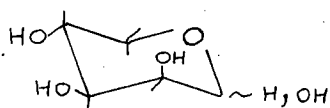


methyl α -D-xylopyranoside

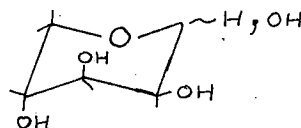


XXII

D-lyxopyranose

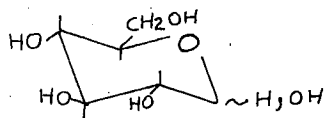


XXIIIa



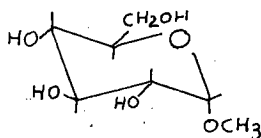
XXIIIb

D-glucopyranose



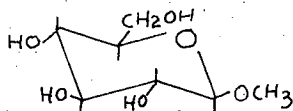
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methyl α -D-glucopyranoside

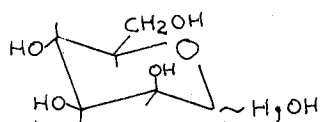


XXV

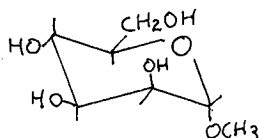
methyl β -D-glucopyranoside



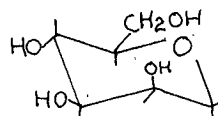
XXVI

D-mannopyranose

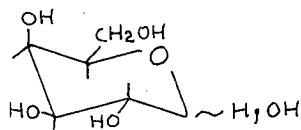
XXVII

methyl α -D-mannopyranoside

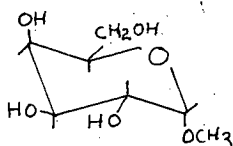
XXVIII

1,5-anhydro-D-mannitol

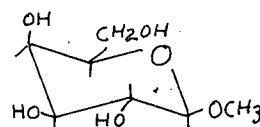
XXIX

D-galactopyranose

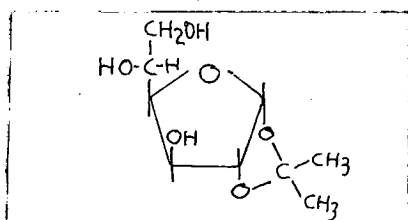
XXX

methyl α -D-galactopyranoside

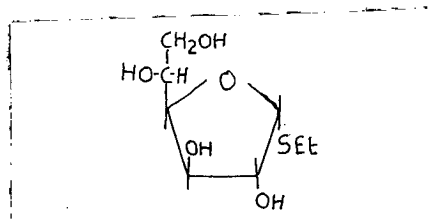
XXXI

methyl β -D-galactopyranoside

XXXII

1,2-O-isopropylidengluco-
furanose

XXXIII

ethyl-1-thio- α -D-glucofuranose

XXXIV

In the following discussion the spectra referred to are those for solutions containing 2M cobalt in which the peaks are better resolved. Again the peaks are labelled A, B, C ... beginning with the lowest field peak.

The contact shifts obtained for the various carbohydrate derivatives indicate that large shifts arise with glucofuranose derivatives and systems which have an axial-equatorial-axial cis,cis triol arrangement.

Of the two inositols studied the contact shifts shown by epi-inositol are much larger than those of myo-inositol, and can easily be explained on the basis that epi-inositol has an axial-equatorial-axial cis,cis triol arrangement (XVIIa) and can thus form a tridentate chelate. Myo-inositol can only achieve such an arrangement in its least favourable conformation (XVIIIb) in which it would have five axial hydroxyl groups out of six. In the alternative conformation of epi-inositol (XVIIb) in which four hydroxyl groups are axial to the ring, two different axial-equatorial-axial triol systems are present and it may be that some chelation whilst in this conformation contributes to the overall averaged contact shift.

With myo-inositol however vicinal bidentate chelation is most probable, and since four equatorial-equatorial and two equatorial-axial hydroxyl pairs exist such complexing as does occur may be distributed over all six possible chelate forms. The resulting averaged contact shifts would thus be much smaller than in epi-inositol where more specific tridentate chelation can occur. The order of contact shifts observed is in accord with the electrophoretic

mobilities in molybdate electrolyte where similar axial-equatorial-axial cis,cis triol complexes are formed.⁹⁶

Of the pentose sugars ribose gives by far the greater shifts, arabinose and lyxose similar shifts and xylose much smaller shifts. In the C 1 conformation (XIXa) α -D-ribose has an axial-equatorial-axial arrangement of hydroxyl groups at positions 1, 2 and 3, and hence could form a tridentate chelate, but the β -anomer could not. However in the alternative 1 C conformation (XIXb) a 2,3,4 tridentate chelate could be formed by both anomers. Formation of such complexes is consistent with the electrophoretic mobility of D-ribose in molybdate electrolyte.⁹⁶

In the 2,3,4 tridentate chelate both H2 and H4 would be axial to their chelate ring and H3 equatorial to both rings whereas in the α -1,2,3 chelate H1 and H3 would be axial, and H2 equatorial to both rings. As noted earlier, protons equatorial to the chelate rings are most strongly shifted. Therefore, if in fact both complexes are formed in solution, then in the 2,3,4 chelate H3 would be most shifted with H2 and H4 less so with the protons on C5 and H1 shifted least, while in the α -1,2,3 chelate H2 would be most shifted with H1 and H3 less so and H4 and the protons on C5 shifted least.

That lyxose shows much smaller shifts than does ribose, they being similar to those of arabinose, is rather surprising in view of its higher electrophoretic migration rate in molybdate solution.⁹⁶ However a tridentate chelate could only be formed by β -D-lyxose and then only in the unfavoured 1 C conformation (XXIIIb), and it may be that the small shifts shown are due to only a small fraction

of the ligand complexing in this form.

In the C 1 conformation (XXIIIa) a β -1,2 bidentate chelate would have H1 equatorial and H2 axial to the chelate ring, but α -1,2 complex formation is impossible as the two hydroxyl groups are trans to each other. 2,3 Complexing would give H3 equatorial and H2 axial, and 3,4 complexing would give both H3 and H4 axial. Thus there exists two possible chelate forms in which there would be a proton equatorial to the chelate ring. If all types of complex formation occur to some degree then H3 would be expected to be shifted the most on average with H1 and H2 shifted less, H4 perhaps even less and both protons on C5 shifted least.

Arabinose and xylose cannot form tridentate chelates in any conformation and so both must form only bidentate chelates. The difference in shifts between them must be due to the difference in conformation at C3. In xylose (XXI) all complexes would have both protons axial to the chelate ring except for an α -1,2 complex which would have H2 equatorial and H1 axial. With arabinose (XX) however the 3,4 chelate as well as the 1,2 chelate would have an equatorial proton, namely that at C3. Thus the lowest field peak in arabinose, peak A, may be assigned to H3, the greater shift compared to xylose being due to its equatorial orientation to the chelate ring. If the shifts given by xylose are corrected to a tert-butanol reference by adding 0.8 p.p.m. and 2.0 p.p.m. for 1M and 2M cobalt respectively (see section 3(V)) then the contact shifts shown are very small, indicating that the degree of complexing is small. This would explain the close similarity of methyl α -D-xyloside to xylose.

Thus it would seem that the configuration at C3 determines the shifts shown, either due to the greater shift of a proton equatorial to the chelate ring or due to a greater degree of complexing occurring with arabinose.

The differences in shifts between lyxose and xylose can then be similarly explained as being due to the difference in configuration at C2. (XXIII, XXI). If 1,2 complex formation is relatively unimportant because of the low basicity of the anomeric hydroxyl then the close similarity in the shifts of lyxose and arabinose is not surprising since the configuration around the molecule in lyxose (XXIII) from C2 to C4 is the same as from C4 to C2 in arabinose (XX). This would also explain the great difference between ribose and lyxose as if 1,2 complexing does not occur then 1,2,3 chelation would also be unlikely. Thus ribose in the 1C confirmation (XIXb) would be the only pentose which could form a tridentate chelate, namely a 2,3,4 chelate.

Of the hexoses glucose and galactose show a lower field peak of intensity two whose shift is virtually unaffected by glycoside formation except that in the methyl glycosides some resolution into two unit intensity peaks occurs, it being more marked for the β -glucoside, but the average shift is almost the same as for peak A in glucose. In mannose however peak A has a greater shift which appears to be somewhat affected by glycoside formation. Thus the lowest field peaks in glucose, galactose and their methyl glycosides probably have a common origin.

Comparison of the relative shifts for the anomeric pairs of

methyl glycosides of glucose and galactose shows that in both cases the β -glycoside shows a slightly greater shift for peak A. However in the case of the glucosides both peak A and peak B are of intensity one whereas for the galactosides peak A is of intensity two and B one. Methyl- α -D-mannoside however shows an inverse ratio to the galactosides, peak A being of intensity one and B of intensity two. The separation between peaks A and B in the spectra is also greater for the β -glycosides but it is interesting that the relative difference is greater for the anomeric glucosides than for the galactosides.

The only difference in configuration between glucose (XXIV) and galactose (XXX) is that at C4, and hence while 2,3 complexing would be the same in a glucoside and the corresponding galactoside, both H2 and H3 being axial to the chelate ring, in a 3,4 complex the galactoside would have H3 equatorial and H4 axial to the chelate ring whereas the glucoside would have both axial. Thus H3 would be shifted more in the galactoside complex than in the glucoside complex. If both 2,3 and 3,4 complexing were occurring then the galactosides would be expected to have peak A of unit intensity and peak B of intensity two. The same would be expected for the glucosides except that peak A would be less shifted. Thus mixed 2,3 and 3,4 complexing cannot explain the observed order of intensities for the glucosides and galactosides.

Mannose (XXVII) and glucose (XXIV) differ only in the configuration at C2, and while 3,4 complexing would be the same in both, in a 2,3 mannoside complex H3 would be equatorial and H2 axial to the

chelate ring, whereas in the corresponding glucoside complex both would be axial. Thus mixed 2,3 and 3,4 complexing would give H3 shifted more in methyl α -D-mannoside than in methyl α -D-glucoside with H2 and H4 of similar shift in both. Thus if approximately equal degrees of 2,3 and 3,4 complexing occurred H2 and H4 would be shifted to about the same extent and so the observed intensities for peaks A and B in the mannoside could be explained on this basis. However that such complexing behaviour cannot explain the order of shifts and peak intensities in the glucosides and galactosides would tend to cast doubt on the validity of this as an explanation of the mannoside results as it might be expected that qualitatively similar behaviour would be shown by all the hexose glycosides studied.

While 4,6 complexing can in principle occur with the hexose glycosides, the orientation of the protons around the chelate ring would differ only for H5, it being axial in the mannoside and glucosides and equatorial in the galactosides. In all chelate rings however H4 and one of the protons on C6 would be axial and the other proton on C6 equatorial to the chelate ring. Thus the shifts in all complexes would be expected to be similar since as shown by butane 1,3 diol the orientation of a proton β to the hydroxyl groups does not appear to affect the relatively small shift experienced. Thus 4,6 complexing would be expected to lead to three single proton peaks, the two most shifted arising from the protons on C6, and so cannot explain the observed spectra, especially the greater separation between peaks A and B in the β -glucoside compared with the α -glucoside.

Similarly monodentate complexing at C6 cannot account for the shift patterns, the protons on C6 being orientated symmetrically with respect to the cobalt even if there is a preferred orientation of the cobalt with respect to the hexose ring.

Thus it can only be concluded that various forms of complexing behaviour occur in these glycosides, the extent of each type probably differing in each. The much smaller shifts given by the glycosides as compared to the polyols is probably due to the fact that stable tridentate complexes cannot be formed, the net result possibly being that an overall smaller degree of complexing occurs.

The much larger shifts obtained with 1,5-anhydromannitol (XXIX) as compared with methyl- α -D-mannoside (XXVIII) indicate a greater degree of complexing in the former. The only difference between the two is that the methoxyl group in the glycoside has been replaced by hydrogen, and so the difference in the degree of complexing may be ascribed to the electron withdrawing nature of the methoxyl group reducing electron availability on the glycoside hydroxyl groups and so the degree of complexing. Precise assignment of all the peaks in the spectrum however required selective replacement studies, preferably replacement of hydrogen by deuterium.

The very large shifts obtained for the glucofuranose derivatives indicate strong specific chelation. With 1,2-O-isopropylidene-D-glucofuranose (XXXIII) 2,3 complexing cannot occur by virtue of substitution at position 2, and also it cannot occur with ethyl-1-thio- α -D-glucofuranoside (XXXIV) as the hydroxyl groups at C2 and C3 are trans to each other in the furanose ring. Hence either 5,6

or 3,5,6 chelation must be occurring.

If 5,6 complexing occurs then one proton on C6 will be equatorial and the other and H5 axial. Thus the equatorial proton would be most shifted, the two axial protons less shifted (and perhaps close to each other) and the remaining four protons much less shifted. In a 3,5,6 complex one proton on C6 and H5 will be equatorial to the five membered ring with the remaining proton on C6 axial, and H3 axial to the six membered ring. Thus the two equatorial protons would be most shifted, and perhaps close to each other, and the axial proton H3 less shifted. Of the remaining three protons H4 would be expected to be shifted rather more than either H1 or H2.

In view of the probability that the large shifts shown by ribose and epi-inositol are due to tridentate chelation 3,5,6 chelation probably also occurs with the glucofuranose derivatives.

While the analysis of the contact shifts obtained on complexing with cobalt is only tentative for the polyols and other carbohydrate derivatives, the shifts of the simpler diols and triols can be analysed virtually completely. The results obtained in this study of cobalt complexes suggest that the system is of interest to organic chemists in a number of ways. Thus selective methylation and deuteration studies should lead to a more complete analysis of the polyol results and, if so, could yield much useful information on the structure and reactivity of the polyols in solution. Similar complete analysis of the carbohydrate complexes would also be of interest.

It is in the field of diols and triols, however, that the contact and pseudocontact shifts produced by complexing with cobalt is of more immediate value. Thus, as has been shown, it is possible to distinguish between diols, specifically between *cis* and *trans* vicinal diols, and to analyse a mixture of diols whose spectra in the absence of cobalt are superimposed. The phenomenon may also be used to determine the position of selective deuteration in various simple compounds possessing a vicinal diol or a 1,2,4 type triol moiety, and also to distinguish between hexafuranose and hexapyranose carbohydrate ring systems. In a section to be presented later (section 3 (VI)) it will also be shown that the method is capable of extension to other types of compounds and other solvent systems.

(f) Mechanism of complex formation and contact shifts

For all the ligands studied only one set of resonances were obtained in the presence of cobalt and hence chemical exchange of ligand between the paramagnetic and the diamagnetic environments must be rapid. Thus the exchange rate must be greater than the reciprocal of the largest value of $\Delta\omega_M$ (the shift in the complex).

That the shifts obtained for *cis* and *trans*-cyclohexane-1,2-diol, *meso* and *racemic*-butane-2,3-diol and propane-1,2-diol are virtually the same at a ligand concentration of 0.5 and 1M indicates that only the cobalt concentration is important and not the actual ligand concentration (see Tables 15, 16, 21-26). The results show that the fraction of ligand complexed is virtually independent of the

ligand concentration for the range of concentrations studied; this can only be so if the fraction of ligand complexed is very small such that the ratio of free to complexed ligand is so large as to be effectively unaltered by relatively small changes in the effective free ligand concentration.

The results of the concentration study with erythritol as ligand at a constant 1M cobalt concentration (see table 33) however appears to show some concentration dependence. However, that the shift increases as the erythritol concentration increases suggests that it is not the erythritol concentration per se that is important else the greatest shift would be obtained at the lowest ligand concentration. Presumably the fact that the solvent concentration decreases as the erythritol concentration increases is responsible for the apparent anomaly, the solvent competing with the ligand for the complexing sites on the cobalt.

The dependence of the shift on the solvent concentration is also of significance in connection with the interpretation of the results given below which are based on the shifts obtained with propane-1,2-diol at a constant molarity (1M) with both cobalt chloride and cobalt perchlorate relative to tert-butanol as reference standard. (see last two sections of table 15).

Table 63.

Conc. Co(II) <u>M</u>	Anion	Peak A	Peak B	Peak C	CH ₃	Shift ratios			Conc. D ₂ O <u>M</u>
		-Δδ ppm	-Δδ ppm	-Δδ ppm	-Δδ ppm	B/A	C/A	CH ₃ /A	
0.50	chloride	2.55	1.09	0.65	0.27	0.43	0.26	0.11	49.4
1.08	"	5.95	2.84	1.45	0.67	0.48	0.24	0.11	48.9
1.53	"	10.38	4.87	2.56	1.19	0.47	0.25	0.11	48.4
2.00	"	15.80	7.44	3.99	1.86	0.47	0.25	0.12	47.3

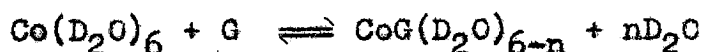
(Contd. P.117)

Table 63 (Contd.)

Conc. Co(II) <u>M</u>	Anion	Peak A $-\Delta\delta$ ppm	Peak B $-\Delta\delta$ ppm	Peak C $-\Delta\delta$ ppm	CH ₃ $-\Delta\delta$ ppm	Shift ratios B/A	C/A	CH ₃ /A	Conc. D ₂ O <u>M</u>
0.51	perchlorate	2.78	1.16	0.71	0.30	0.42	0.25	0.11	48.0
1.00	"	6.75	3.13	1.66	0.76	0.46	0.25	0.11	46.3
1.52	"	13.7	6.04	3.34	1.57	0.44	0.24	0.11	43.6
2.04	"	obscured	9.77	5.66	2.70				42.1

Whilst the actual shifts are significantly different for cobalt chloride and cobalt perchlorate the very close similarity in the shift ratios suggests that the type of complexing is the same for both salts. In fact the differences in the actual shifts are greatly decreased when the shifts are normalised to take into account the different solvent molarities. The normalisation procedure used was to multiply the observed shifts by $[\text{solvent}]^n / [55.9]^n$, where 55.9 is the molarity of pure deuterium oxide and n is an integer, i.e. normalised to pure solvent.

Considering the replacement of solvent in hydrated cobalt by a glycol (G) the equilibrium equation can be written as



In this equation n is the number of solvent molecules displaced and could have any value up to six. The equilibrium constant is then given by

$$K = \frac{[\text{CoG}(\text{D}_2\text{O})_{6-n}][\text{D}_2\text{O}]^n}{[\text{Co}(\text{D}_2\text{O})_6][\text{G}]}$$

If the degree of glycol complexing is very small then the concentration of hydrated cobalt and glycol may be approximated by their actual total concentrations and are effectively constant. The

concentration of glycol complexed is then given by

$$[\text{CoG}(\text{D}_2\text{O})_{6-n}] = K' / [\text{D}_2\text{O}]^n \text{ where } K' = K / [\text{Co}(\text{D}_2\text{O})_6][\text{G}]$$

and so is inversely proportional to the solvent concentration. Thus the greater the solvent molarity the smaller the fraction ligand complexed, and so the smaller the recorded shift. Thus, in order to take into account the different solvent concentrations in the various solutions the normalising factor of $[\text{solvent}]^n / [55.9]^n$ was introduced. In this factor, since the cobalt is assumed to have six hydration molecules in the equilibrium equation the effective solvent concentration is given by the total solvent molarity as given in table 63 minus six.

Normalising for the value $n = 1$ the cobalt chloride shifts were still significantly smaller than those for cobalt perchlorate, but for values of n equal to or greater than three the chloride shifts become greater than the perchlorate shifts, becoming more so with increasing values of n . Normalising for $n = 2$ the results given below were obtained (table 64).

Table 64.

Conc. Co(II) <u>M</u>	Anion	Peak A (norm.) - $\Delta\delta$ ppm	Peak B (norm.) - $\Delta\delta$ ppm	Peak C (norm.) - $\Delta\delta$ ppm	CH ₃ (norm.) - $\Delta\delta$ ppm
0.50	chloride	1.54	0.66	0.39	0.16
1.08	"	3.51	1.68	0.86	0.40
1.53	"	5.99	2.80	1.48	0.69
2.00	"	8.66	4.07	2.18	1.19
0.51	perchlorate	1.58	0.66	0.40	0.17
1.00	"	3.53	1.64	0.88	0.40
1.52	"	6.22	2.75	1.52	0.71
2.04	"	obscured	4.08	2.36	1.13

Considering the crudity of the method, especially that of calculating the deuterium oxide concentration (see footnote d table 15), the agreement between the two sets of values is good, and the finding that $n = 2$ is in accord with chelate formation since two molecules of solvent are then replaced by one molecule of propane-1,2-diol.

Thus the actual shift will depend on the fraction of ligand complexed, (which in turn is dependent on the ligand co-ordination number and solvent molarity) and on the contact shift of the proton in the complex. Further, it is clear that the fraction of ligand complexed in the ligands studied is so small as to be virtually independent of ligand concentration, although this may no longer be true at very low ligand and high cobalt concentrations.

Considering now the complex itself, it has been shown in the preceding discussion of the contact shifts that both contact and pseudocontact shifts may be important in the systems studied. Before considering the results of variable frequency and variable temperature studies, it will first be instructive to consider the effect of these variables on the Swift and Connick equations. The temperature effects have already been discussed in section 2 (V), and the effects of frequency will now be considered.

Case A $(\Delta\omega_M)^2 \gg (1/T_{2M})^2, (1/\tau_M)^2$

$$1/T_{2p} = f/\tau_M \quad \text{_____} \quad (19)$$

$$\Delta\omega = f/\tau_M^2 \Delta\omega_M \quad \text{_____} \quad (20)$$

Thus increase in frequency will decrease the shift whilst the line width will be unaffected and governed by the rate of chemical

exchange.

Case B $(1/\tau_M)^2 \gg (\Delta\omega_M)^2 \gg 1/T_{2M}\tau_M$

$$1/T_{2p} = f\tau_M\Delta\omega_M^2 \quad \text{_____} \quad (21)$$

$$\Delta\omega = f\Delta\omega_M \quad \text{_____} \quad (22)$$

Thus both the line width and the shift will increase with increasing frequency but the line width will increase faster and so resolution will be poorer at higher frequencies.

Case C $(1/T_{2M})^2 \gg (\Delta\omega_M)^2, (1/\tau_M)^2$

$$1/T_{2p} = f/\tau_M \quad \text{_____} \quad (23)$$

$$\Delta\omega = f\Delta\omega_M T_{2M}^2/\tau_M^2 \quad \text{_____} \quad (24)$$

Thus the shift will probably increase with increasing frequency, although the precise magnitude of any effect will depend on the relative contribution of the scalar term in the expression for T_{2M} in equation (12). The line width however will be unaffected by frequency increase.

Case D $1/T_{2M}\tau_M \gg (1/T_{2M})^2, (\Delta\omega_M)^2$

$$1/T_{2p} = f/T_{2M} \quad \text{_____} \quad (25)$$

$$\Delta\omega = f\Delta\omega_M \quad \text{_____} \quad (26)$$

Whilst the shift will increase with increasing frequency the effect on the line width will depend on the effect of frequency on T_{2M} .

As previously noted (see section 2(IV)(c)), due to the very short electron relaxation time the expression for the relaxation times in a cobalt complex is given by

$$\frac{1}{T_{1M}} = \frac{1}{T_{2M}} = \frac{4}{3} \frac{S(S+1)g^2\beta^2\gamma_I^2}{\gamma^6} \cdot \tau_s + \frac{4}{3} \frac{S(S+1)A^2}{\hbar^2} \cdot \tau_s \quad \text{_____} \quad (13)$$

Examination of equation (13) shows that it contains no frequency term whereas if the shift is expressed such that the units are c/s and not ppm then the shift given by equation (1) does have a frequency term. Thus T_{2M} will be independent of frequency whilst $\Delta\omega_M$ will be directly proportional to the frequency.

Since the spectra obtained in the presence of Co(II) show differential broadening (see section 3 (III)) then chemical exchange cannot be controlling the line widths. Hence cases A and C cannot be the dominant mechanisms for this system. The requisite expressions for shift and line width are thus those of cases B or D.

By considering the relationship between line width and shift a possible method of distinguishing between the two fast exchange cases B and D may be obtained.

For case B:

$$\frac{1/T_{2P}}{\Delta\omega} = \frac{f\tau_M\Delta\omega_M^2}{f\Delta\omega_M} = \tau_M\Delta\omega_M \quad (27)$$

According to the limiting conditions this must be very much less than one.

For case D:

$$\frac{1/T_{2P}}{\Delta\omega} = \frac{f}{T_{2M}} \cdot \frac{1}{f\Delta\omega_M} = \frac{1}{\Delta\omega_M T_{2M}} \quad (28)$$

The limiting conditions in this case do not forbid this being either greater or less than one. Thus if the line width to shift ratio is greater than unity then case B control cannot be dominant and so case D control must be the dominant mechanism, but if the ratio is less than unity no clear distinction can be made.

In view of the large shifts obtained for the most shifted peaks, for these peaks at least $\Delta\omega_M$ must be large, and so the possibility exists that for these peaks some measure of τ_M control (case A) might be involved. In this context it is instructive to consider the relationship between the line width and the square of the observed shift as the resonance frequency and hence $\Delta\omega_M$ is increased.

For case A:

$$\frac{1/T_{2P}}{\Delta\omega^2} = \frac{f\tau_M^4\Delta\omega_M^2}{\tau_M f^2} = \frac{\tau_M^3\Delta\omega_M^2}{f} \quad (29)$$

According to the limiting conditions the line width will increase more rapidly than the square of the shift as the frequency is increased.

For case B:

$$\frac{1/T_{2P}}{\Delta\omega^2} = \frac{f\tau_M\Delta\omega_M^2}{f^2\Delta\omega_M^2} = \frac{\tau_M}{f} \quad (30)$$

Under given conditions this will remain constant.

For case C:

$$\frac{1/T_{2P}}{\Delta\omega^2} = \frac{f\tau_M^4}{\tau_M f^2\Delta\omega_M^2 T_{2M}^4} = \frac{\tau_M^3}{f\Delta\omega_M^2 T_{2M}^4} \quad (31)$$

Since T_{2M} and τ_M are independent of frequency this will decrease with increasing frequency.

For case D:

$$\frac{1/T_{2P}}{\Delta\omega^2} = \frac{f}{T_{2M} f^2 \Delta\omega_M^2} = \frac{1}{f T_{2M} \Delta\omega_M^2} \quad (32)$$

Again, since T_{2M} is independent of frequency this ratio will decrease with increasing frequency.

Thus equations (27) to (32) taken in conjunction may be used to

distinguish between case B and case D control and the extent of case A contribution for the most shifted peaks.

For a solution 1M in both propane-1,2-diol and cobalt chloride the following results were obtained at a constant temperature of 33.5°C (probe temperature). The shifts were obtained relative to tetramethylammonium chloride as internal standard but have been corrected to a non-shifted tert-butanol standard as given in section 3(V).

Table 65.

Frequency M c/s	Peak A			Peak B		
	$-\Delta\delta$ ppm	$-\Delta\delta$ c/s	$\Delta\nu$ 1/2c/s	$\Delta\delta$ ppm	$\Delta\delta$ c/s	$\Delta\nu$ 1/2c/s
40	6.0	240	13.0	2.9	156	14.2
60	6.0	360	29.1	2.9	174	24.9
100	6.2	620	64	3.0	300	33

Table 65 (Contd.)

Frequency M c/s	Peak C			CH ₃		
	$-\Delta\delta$ ppm	$-\Delta\delta$ c/s	$\Delta\nu$ 1/2c/s	$-\Delta\delta$ ppm	$-\Delta\delta$ c/s	$\Delta\nu$ 1/2c/s
40	1.4	56	12.9	0.7	28	4.9
60	1.5	90	23.7	0.7	42	10.2
100	1.5	150	29	0.8	80	15

In order to obtain the value of $1/T_{2p}$ from the measured line width the natural line width in the diamagnetic solution (taken as 1.0 c/s) must be subtracted. In the table below this has been done and the shift in c/s used in calculating the ratios.

Table 66

Frequency M c/s	Peak A		Peak B	
	$(1/T_{2p})/\Delta\omega$	$(1/T_{2p})/\Delta\omega^2$	$(1/T_{2p})/\Delta\omega$	$(1/T_{2p})/\Delta\omega^2$
40	5.0×10^{-2}	2.1×10^{-4}	8.4×10^{-2}	5.4×10^{-4}
60	7.8×10^{-2}	2.2×10^{-4}	13.7×10^{-2}	7.9×10^{-4}
100	10.3×10^{-2}	1.7×10^{-4}	11.0×10^{-2}	3.7×10^{-4}

Table 66 (Contd.)

Frequency M c/s	Peak G		CH_3	
	$(1/T_{2p})/\Delta\omega$	$(1/T_{2p})/\Delta\omega^2$	$(1/T_{2p})/\Delta\omega$	$(1/T_{2p})/\Delta\omega^2$
40	21.2×10^{-2}	37.9×10^{-4}	13.9×10^{-2}	49.7×10^{-4}
60	25.2×10^{-2}	28.0×10^{-4}	21.9×10^{-2}	52.2×10^{-4}
100	19.3×10^{-2}	12.9×10^{-4}	18.8×10^{-2}	23.4×10^{-4}

The remarkable consistency of the figures in the second column for peak A in table 66 above, especially between 40 and 60 M c/s indicates that there is very little or no case A τ_M control contribution (c.f. equation 29), and since this is the most shifted peak there cannot be any τ_M control contribution for any of the other peaks. The controlling mechanisms are thus case B and case D. The consistency of the ratio also indicates that for peak A at least equation (30) is obeyed and hence the controlling mechanism for this peak is predominantly case B. This can be confirmed by multiplying the 40 Mc/s width to shift ratio by 6/4 and 10/4 whence the values obtained are 7.5 and 12.5×10^{-2} respectively in comparison with the experimental values of 7.8 and 10.7×10^{-2} for the 60 Mc/s and 100 Mc/s ratios respectively. The inconsistencies in both ratios for all other peaks however are such that neither case B nor case D

control can explain them.

The difference between $\Delta\omega_M$ and T_{2M} determine whether case B or case D control will operate, the former if $\Delta\omega_M$ is much larger than $1/T_{2M}\tau_M$. Hence case B control is more likely to be favoured for the most shifted peak as is found. When the relationship between $\Delta\omega_M$ and T_{2M} is unknown, another form of the Swift and Connick equation may be obtained which is essentially a combination of both cases.

Case E $(1/\tau_M)^2 \gg (\Delta\omega_M)^2 + 2/T_{2M}\tau_M$

$$\frac{1}{T_{2p}} = \frac{f}{T_{2M}} + f\tau_M\Delta\omega_M^2 \quad (33)$$

and, $\Delta\omega = f\Delta\omega_M \quad (34)$

Hence $\frac{1/T_{2p}}{\Delta\omega} = \tau_M\Delta\omega_M + \frac{1}{T_{2M}\Delta\omega_M} \quad (35)$

and $\frac{1/T_{2p}}{\Delta\omega^2} = \frac{\tau_M}{f} + \frac{1}{fT_{2M}\Delta\omega_M^2} \quad (36)$

Thus both the shift and the line width will increase with increasing frequency, but the effect of frequency on the two ratios given by equations (35) and (36) will depend on the relative contributions of the two terms in the equations, and so on the relative extent of case B and case D control.

The case B term will tend to become of more importance as the frequency increases since as $\Delta\omega_M$ increases case B control will tend to increase, but will be of relatively little importance for peaks exhibiting small shifts. For the peaks in the spectrum other than Peak A the combined mechanisms as given by equations (33) and (34)

are probably operative.

A variable temperature study was also performed at 100 Mc/s with the results given below. The τ values listed are based on the tetramethylammonium ion as being 6.83τ in a solution 1M in propane-1,2-diol and cobalt chloride.

Table 67

Temp. °C	Peak A τ	$\Delta\nu$ 1/2c/s	Peak B τ	$\Delta\nu$ 1/2c/s	Peak C τ	$\Delta\nu$ 1/2c/s	CH ₃ τ	$\Delta\nu$ 1/2c/s
13	c.a.-0.7	c.a. 200	2.31	78	3.51	40	6.8	-
33.5	-0.4	64	2.80	33	3.80	29	7.29	15
72	0.14	33	3.24	34	3.96	30	7.60	18

That differential broadening is still shown at the lowest temperature indicates that chemical exchange is still rapid enough to be outwith the range of τ_M control (case A). The very large line width of peak A at the lowest temperature and the fact that the line width decreases regularly with increasing temperature (whereas for the other peaks no further decrease is shown much above 30°C) tends to confirm the conclusion that peak A is almost completely case B controlled whereas the others are a mixture of case B and case D control. The decrease in shift with increasing temperature noted is in accord with the predicted temperature dependence as given by equation (1). However these conclusions must be tentative since change in temperature will alter the degree of complexing.

Thus, in conclusion, the contact shift and line broadening mechanisms appear to be a combination of the Swift and Connick case B and case D control mechanisms, with the relative contribution

of case B control increasing as the shift increases; peak A in propane-1,2-diol being almost completely case B controlled. The recorded, averaged shift is dependent on the fraction of ligand complexed which is in turn dependent on the degree of competition from the solvent, and on the shift in the complexed species. Any contributions from mixed complexes between ligand and chloro-complexes of cobalt seem to be relatively unimportant as indicated by the agreement between the shifts obtained for propane-1,2-diol with cobalt chloride and cobalt perchlorate when the differences in solvent concentrations are compensated for.

(V) Internal referencing in concentrated cobalt solutions

In the course of studies of cobalt complexes in acetone solution it was observed that relative to tetramethylsilane (TMS) the solvent acetone peak showed an upfield shift on addition of cobalt. Since acetone showed an apparent downfield shift relative to tetramethylammonium chloride in aqueous solution this observation thus cast doubt on the validity of the tetramethylammonium ion as an internal reference standard. Consequently various possible internal references were studied in the presence of cobalt in various solvent systems.

In acetone solution, relative to TMS, dioxan showed a downfield shift on addition of cobalt perchlorate, the magnitude of which was dependent on both the cobalt and the water concentration as shown in

Table 68. The water concentration given below includes that from the six water molecules associated with the cobalt. Cobalt perchlorate was used as this in acetone solution gives the normal pink coloured solution associated with octahedrally co-ordinated cobalt whereas cobalt chloride gave the blue coloured solution associated with tetrahedrally co-ordinated cobalt, showing that complexing with chloride was occurring. The dioxan concentration was one molar.

Table 68

Conc. $\text{Co}(\text{ClO}_4)_2$ <u>M</u>	Conc. H_2O <u>M</u>	Dioxan τ	ΔV 1/2c/s	Acetone τ
nil	nil	6.42	1.5	7.93
0.26	1.5	5.75	9.8	8.4
0.26	4.6	6.28	3.1	8.09
0.26	7.5	6.37	2.9	7.95
0.51	3.0	5.05	20.6	8.80

Thus in the absence of a competing ligand dioxan shows a quite substantial downfield shift and acetone an upfield shift. Above 8M water, i.e. a water to cobalt ratio of about sixteen, dioxan appears unaffected.

A study with tert-butanol gave similar results (table 69), the concentration of tert-butanol being one molar.

Table 69.

Conc. $\text{Co}(\text{ClO}_4)_2$ <u>M</u>	t-BuOH τ	Acetone τ
nil	8.80	7.9
0.14	7.48	8.0
0.25	0.09	8.2
0.49	-2.14	8.5

In this study no added water was present, and the results indicate that tert-butanol can co-ordinate quite strongly with cobalt if no other competing ligand is present in any great concentration.

In order to determine the shifts of dioxan, tert-butanol and tetramethylammonium chloride together relative to TMS similar studies were carried out, this time in aqueous methanol solvent. The studies were done both in the presence and in the absence of 1M propane-1,2-diol in order to determine the effect of any competing ligand. Aqueous methanol was chosen as the solvent as of the possible aqueous-organic solvent systems this was the closest to pure water. The water concentrations listed in table 70 include the hydration water of the cobalt salt weighed out. The concentrations of the various reference standards were all between 0.2 and 0.3M.

Table 70.

Conc. Cobalt M	Cobalt Salt	Conc. H ₂ O M	Conc. methan- ol M	Dioxan τ	tert- butan- ol τ	tetra- methyl- ammonium τ	propane- 1,2-diol
nil	chloride	7.1	18.3	6.27	8.76	6.76	present
1.02	"	12.0	15.4	6.48	8.77	7.88	"
1.51	"	14.4	13.8	6.54	8.79	8.45	"
1.00	"	12.6	17.5	6.40	8.71	7.61	absent
1.51	"	15.1	15.7	6.40	8.70	8.12	"
Nil	perchlorate	7.1	18.3	6.30	8.75		present
0.99	"	11.8	15.1	6.41	8.75		"
1.52	"	13.9	12.4	6.35	8.75		"
1.01	"	12.4	16.6	6.32	8.67		absent
1.52	"	14.6	14.1	6.14	8.57		"

Of the three possible reference standards examined tert-butanol would appear to be the best one, although it too shows a down-

field shift if no glycol ligand is present. The shifts obtained with dioxan are very interesting in that this compound shows both positive and negative shifts, negative being shown in the absence of competing ligand in acetone and in one instance above. The most probable explanation for this behaviour is that when dioxan replaces water in the cobalt co-ordination sphere delocalisation occurs to some extent in the normal way leading to downfield shifts. The presence of another more strongly co-ordinating ligand would reduce such dioxan co-ordination, and so reduce the downfield shift experienced as was found (Table 68). In such a situation hydrogen bonding between dioxan and the first co-ordination sphere water molecules could however occur and this could give rise to upfield shifts through pseudocontact interactions. Such hydrogen bonding to the co-ordination sphere water could also explain the upfield shifts given by acetone.

The tetramethylammonium ion however is consistent in that it gives large upfield shifts irrespective of whether propane-1,2-diol is present or not. In the solutions containing cobalt chloride, judging from the deep blue colour of the solution, at least a substantial portion of the cobalt exists in the tetrahedrally co-ordinated form, probably as a chloro-complex, and hence the upfield shifts of the tetramethylammonium ion could have arisen from ion-pairing with a negatively charged chloro-cobalt species. As has been noted in the introduction, protons involved in an ion-pair involving a paramagnetic ion can incur substantial pseudocontact shifts, and the tetramethylammonium shifts in the cobalt chloride

solution might be due to a similar ion-pair formation. Unfortunately the effect of a hexa-co-ordinated cobalt species could not be tested in this system using cobalt perchlorate as tetramethylammonium perchlorate is only sparingly soluble under such conditions.

However the shifts incurred by the tetramethylammonium ion in aqueous cobalt chloride solutions were obtained relative to tert-butanol by comparing the spectra of cobalt solutions of various ligands with only tetramethylammonium chloride added and then re-run after addition of tert-butanol as shown in table 71. Comparison of the separation between the various ligand peaks and the tetramethylammonium peak before and after addition of tert-butanol showed that the addition of tert-butanol made negligible difference to the shifts. The results obtained are given in table 71 with the shifts incurred by the tetramethylammonium ion being calculated on the assumption that the tert-butanol was not shifted. With the solutions containing only tert-butanol as ligand a direct comparison was obtained.

Table 71.

Ligand and ligand conc.	Conc. CoCl_2 <u>M</u>	Me_4N^+ $\Delta\delta$ ppm
methanol (<u>1M</u>)	1	+0.70
	2	+1.94
2-methoxy ethanol (<u>1M</u>)	1	+0.80
	2	+1.94
ethylene glycol (<u>1M</u>)	1	+0.78
	2	+1.94
racemic-butane-2, 3-diol (<u>1M</u>)	1	+0.92
	2	+2.27

(Contd. P.132)

Table 71 (Contd.)

Ligand and ligand conc.	Conc. CoCl_2 <u>M</u>	Me_4N^+ $\Delta\delta$ ppm
propane-1,2-diol (<u>1M</u>)	0.5	+0.30
	1	+0.80
	1.5	+1.38
	1	+0.97
	2	+2.33
<u>tert</u> -butanol (<u>1M</u>)	1	+0.86
	2	+1.94
<u>tert</u> -butanol (<u>0.3M</u>)	1	+0.80
	2	+1.94

The average shifts of the tetramethylammonium ion relative to tert-butanol for various cobalt concentrations thus obtained are as follows:

Table 72

Conc. CoCl_2 <u>M</u>	$\Delta\delta \text{Me}_4\text{N}^+$ ppm		Average
	Maxm.	Minm.	
0.5	+0.30	+0.30	+0.30
1	+0.97	+0.70	+0.83
1.5	+1.38	+1.38	+1.38
2	+2.33	+1.94	+2.04

If the tert-butanol is shifted slightly downfield this would have the effect of making the apparent tetramethylammonium shift correspondingly larger than the true shift. In view of the possibility that tert-butanol may be in fact shifted slightly downfield the corrections to be applied to correct the shifts relative to the tetramethylammonium ion to those relative to a "non shifted" tert-butanol reference were thus taken as 0.8 ppm (+0.1) and 2.0 ppm (+0.2)

for 1M and 2M cobalt respectively.

If, as would seem most likely, the proportion of chloro cobalt species is very small in aqueous solution, especially negatively charged species, then the large upfield shifts shown by the tetramethylammonium ion cannot be due to pseudocontact shifts arising from ion pair formation. A possible explanation may be that repulsion effects between the two positively charged species produce a situation in which the bulk susceptibility in the vicinity of the tetramethylammonium ion is significantly different from that in the region of the other species in the solution as a whole, the upfield shifts then being bulk susceptibility shifts. Alternatively ion triplets of the type $\text{Co}^{++} \cdots \text{Cl}^- \cdots \text{NMe}_4^+$ may be involved.

While tert-butanol appears to be the most satisfactory internal reference standard, the conclusion from the results shown in the preceding tables is that in general, for concentrated cobalt solutions a "true" internal reference standard does not exist. This conclusion is probably also valid for concentrated solutions of other similar paramagnetic ions. Furthermore the use of external reference standards does not seem promising in view of the magnitude of the bulk susceptibility corrections which would be required.

(VI) Other systems - preliminary studies

In order to test the feasibility of extending the use of the contact shifts produced by complexing with cobaltous ion two other systems have been briefly investigated. In aqueous solution two salts, sodium gluconate and sodium propionate have been studied, and some simple alcohols have been studied in dry acetone solution.

With the two salts very large shifts were obtained, especially for the gluconate ion where chelation through both hydroxyl and carboxyl groups can occur. The concentration of the salts was one molar in each case, and the results are referred to the tetramethylammonium ion as being 6.83τ and so are uncorrected. Sodium propionate being slightly alkaline, some precipitation occurred in this case at high cobalt concentrations.

Table 73. sodium gluconate $\text{CH}_2\text{OH}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CO}_2^-\text{Na}^+$

Conc. CoCl_2 $\underline{\text{M}}$	Peak A(=1H)		Peak B(=1H)		Peak C(=1H)	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s$
Nil	5.90		5.90		6.25	
0.25	-9.08	86	-9.08	86	6.20	
0.5	-19.5	140	-19.5	140	6.03	
1.0	-31.4		-29.6		2.83	62
2.0	-48		-39		-6.7	

Table 73 (Contd.)

Conc. CoCl_2 $\underline{\text{M}}$	Peak D(=2H)		Peak E(=1H)		OH	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s$
Nil	6.25		6.25		5.32	1.3
0.25	6.39		6.53		4.70	18
0.5	6.04		6.3		3.35	37
1.0	4.80	57	6.12	29	-0.93	72
2.0	-0.4		3.5		-10.9	

Table 74. sodium propionate

Conc. CoCl ₂ <u>M</u>	CH ₂		CH ₃		OH	
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}$
Nil	7.84	1.2	8.98	1.4	5.33	1.0
0.125	4.6	—	6.01	—	4.5	—
0.25	1.79	24.3	6.50	15.4	3.56	15.1
0.5	-2.59	26.1	4.69	15.7	1.62	28.3
cal ^a	-7.47	31	2.54	16.5	-2.51	51
ca2	-15.79	32	-1.36	19.2	-11.93	93

(a) some precipitation soon after making up solutions.

The large difference in shift between protons situated near to, or in the case of chelation between, and those far removed from binding sites indicates the usefulness of this method in studying the type of binding in acids and hydroxy acids. In the case of fatty acids the shift experienced by the α -protons will be directly proportional to the extent of complexing of the ligand, and so by working under standard conditions the method could be used to obtain a correlation between the donor strengths of various carboxylate ions.

The aqueous solvent system used in the present work on alcohols and polyols is of limited application as only water-soluble substances can be studied, and in order to extend the use of the cobalt system preliminary investigation of an acetone solvent system has been carried out. Cobalt chloride is quite readily soluble in acetone up to about 0.5M, but in compensation for limited solubility the shifts obtained are much larger than in aqueous solution. A serious drawback however is that cobalt chloride forms tetrahedral chloro complexes in acetone solution and so the exact co-ordination system is uncertain.

Cobalt perchlorate in acetone exists as an octahedrally coordinated system in acetone however and so is more amenable to study. In this system simple alcohols gave substantial shifts whose magnitude was dependent on both cobalt concentration and on the amount of water present. The most serious drawback however is that at low water concentrations the shifts are strongly dependent on the amount of water present while at water concentrations above about ten per cent the shifts obtained using 0.25 - 0.5 M cobalt perchlorate are rather small.

Anhydrous acetone can be obtained by drying over molecular sieves and anhydrous cobalt perchlorate by addition of silver perchlorate to an acetone solution of anhydrous cobalt chloride (dried by treatment with 2,2-dimethoxypropane).⁵⁶ An anhydrous system thus presents no major experimental problems. In this manner ligands, especially strongly binding ligands, can be studied both in a stoicheometric complex and over concentration range of excess ligand so enabling shifts in the complex species to be obtained and exchange effects to be studied. Analysis of the shifts in the complex would yield valuable information about co-ordination sites and types of binding. In such a system competing solvent effects are minimised, and exchange phenomena can be studied down to quite low temperatures so yielding information about preferred co-ordination sites in ligands with more than one possible co-ordination site such as hydroxy acids.

Ligands such as nitriles, iso-nitriles and thiocyanate could also be studied in such a system, and in this connection it is

interesting that ethylcyanide gave positive, upfield shifts for both the methylene and the methyl group with cobalt perchlorate in acetone solution, indicating that a spin polarisation mechanism is probably operative.

By using cobalt acetylacetonate the system can also be extended to chloroform soluble ligands, giving a complex system of known geometry in which pseudocontact shifts can give insight into the geometry of the complex and so of the co-ordination behaviour of the ligands. Preliminary studies in this system with alcohols and amines as ligands showed that substantial shifts can be obtained, the interesting point being that for both ethanol and diethyl amine the methylene group showed fairly large downfield shifts whereas both the hydroxyl and the amino proton were shifted upfield.

Thus the potential information which can be derived from studies of complexing with cobalt compounds extends over a wide range of possible ligands.

PART 4: SELECTIVE BROADENING OF THE N.M.R. SPECTRA OF
SULPHIDES BY COPPER (II)

(I) Introduction

(a) General Introduction

In this section a study of selective broadening of the N.M.R. spectra of certain thio ethers by copper (II) is described. This work arose out of a chance observation; on one occasion the N.M.R. spectrum of 1,2,3,4-tetra-O-acetyl-6-deoxy-6-thiomethyl- β -D-glucopyranoside was found to contain two unexpectedly broad peaks and further investigation revealed that accidental contamination by copper (II) must have been responsible for this effect. Studies with diethylsulphide revealed that whilst copper (II) produced marked selective broadening of the N.M.R. signals of the methylene group, the series of ions iron (II), iron (III), manganese (II), nickel (II), cobalt (II) and chromium (III) had virtually no effect on the N.M.R. spectrum, the effect being peculiar to copper.

The most interesting point arising from these studies was that while the methylene group in diethylsulphide showed in the spectrum as a very broad singlet mass when significant amounts of copper were present, the methyl peak still showed clear triplet splitting indicating that the protons were still coupled with those of the methylene group. This was found to be a general phenomenon for all $-S-CH_n-CH_m-$ groupings in which even although the CH_n group next to the sulphur was much broadened the CH_m group still remained coupled to it and showed fine structure arising from this coupling. This point is discussed further in section 4 (III)(b). Similar

addition of Cu(II) to the corresponding oxygen ethers however produced no measurable line broadening.

Since complex formation with the copper is undoubtedly involved, the complexing behaviour of sulphur containing ligands will be discussed briefly.

(b) Complexes of sulphur containing ligands

In general, sulphur containing ligands form stronger complexes than the corresponding oxygen containing ligands with many ions,⁹⁷ but thio ethers only form isolable complexes with B type central ions such as the platinum series and mercuric ions whilst the copper (II) and nickel (II) complexes are either very unstable or non existent.⁹⁸

Relatively stable thio ether complexes are formed by many heavy metal halides;⁹⁹ the stability of the ruthenium complexes depending on the halide, being greater for the chloride and least for the iodide complexes.¹⁰⁰ Whilst no thio ether complexes of first transition series ions have been isolated in a relatively stable form it has been shown that cobalt (II) forms complexes with dialkyl sulphides in solution, a deep blue colour being obtained when cobalt salts are added to the neat sulphide.¹⁰¹ However by using the chelate effect cobalt (II)¹⁰¹ and nickel (II)¹⁰² complexes with 2,5-dithiahexane and 3,6-dithiaoctane have been prepared, although even so they were only moderately stable.

Various complexes with 1,4-dithiane and 1,4-thioxane have been prepared,^{97b,103} including those with copper (II),¹⁰⁴ and infrared

studies have shown that in both ligands bonding occurs through the sulphur atom.¹⁰⁵ Preferential co-ordination through the sulphur atom in 1,4-thioxane has also been shown by N.M.R. studies of the titanium and zirconium complexes.¹⁰³ A similar N.M.R. study has been made of diethyl sulphide complexed with iridium (III) salts,¹⁰⁶ and the complex $[\text{Ag}(\text{pyridine})_2]\text{-trans-}[\text{Ir}(\text{Et}_2\text{S})_2\text{Cl}_4]$ gave the very interesting result that whilst the single methyl resonance obtained was sharp the methylene resonance was very weak and broad, this being attributed to the presence of traces of paramagnetic iridium (IV) in the diamagnetic iridium (III) salt used.

Thus whilst in general isolable complexes with sulphur ligands are only formed with group B^{97a} ions, unstable complexes can be formed in solution by first series transition ions, and, if the extra stability conferred by chelation is utilised, complexes of such ions may be isolated.

(II) Experimental

(a) Standard Conditions

All spectra were obtained using a Perkin-Elmer model R10 60Mc/s spectrometer at a probe temperature of 33.5°C. Unless otherwise stated all solutions were one molar in ligand; 500 μ l of each ligand solution was added to the N.M.R. sample tube and then, just before running the spectrum, the appropriate volume of a stock solution of copper (II) added from a micro syringe and the two mixed by shaking. This procedure was used since it was found that 'fading' occurred more or less rapidly on adding copper, the copper (II) being reduced to copper (I).

The stock copper solutions were prepared by weighing out the appropriate weight of the copper salts. In some cases copper (II) was added as tetrahalocuprate salts (see following section); these were dissolved in chloroform to give a stock solution of approximately 0.1M strength. Cupric chloride dihydrate and cupric bromide were dissolved in methanol to give stock solutions of approximately 0.05M strength.

With each ligand, for each different addition of copper, the spectrum was re-run at intervals in order to measure the relative rate of removal of copper (II) from the solution. Where measurement was made over extended intervals the solutions were stored in the dark in the sample tube.

The chloroform used as solvent was first freed from ethanol by passage through a silica column.

(b) Preparations

bis-(tetra-n-butylammonium)-tetrabromocuprate.

Tetra-n-butylammonium bromide (6.45g.) in ethanol was added to a solution of cupric bromide (2.24g.) in ethanol, and the ethanol then removed in vacuo until a thick black syrup was obtained. Benzene was then added until precipitation began and then after 2 hrs. at -5°C the purple precipitate filtered off. The crude product was then recrystallised from 100 ml. of a 10% ethanol in benzene solution.

Yield 6.11g. (70% based on cupric bromide) as soft purple clumps.

m.p. 82 - 84°C

(Found: C, 45.1; H, 7.9; Br, 34.3. $C_{32}H_{72}N_2CuBr_4$ requires
C, 44.3; H, 8.4; Br, 36.8%)

tetra-n-butylammonium chloride.

Tetra-n-butylammonium iodide (6.29g.) in water was shaken with a large excess of freshly precipitated silver chloride for 2 hrs. and then the mixture filtered and the precipitate washed with water. The combined filtrate and washings were evaporated in vacuo at 40°C, and the residue dried by repeated evaporation with iso-propyl alcohol and then recrystallised from petroleum ether-benzene.

Yield 2.82g. (60%). Hygoscopic white solid m.p. 88-90°C.

Literature m.p. 92.5 - 94.2°C.¹⁰⁷

bis-(tetra-n-butylammonium)-tetrachlorocuprate

Tetra-n-butylammonium chloride (2.8g.) in ethanol was added to an ethanolic solution of cupric chloride dihydrate (0.86g.) and the solution evaporated in vacuo to give a brownish-red syrup. Addition of benzene and shaking produced crystallisation. The crude product was then recrystallised from 10% ethanol in benzene.

Yield 3.06g. (88% based on cupric chloride) as golden yellow clumps. m.p. 110°C.

(Found: C, 55.0; H, 10.4; Cl, 19.2. $C_{32}H_{72}N_2CuCl_4$ requires C, 55.7; H, 10.5; Cl, 20.5%).

4-tert-butylcyclohexanone.

This was prepared by dichromate oxidation of 4-tert-butylcyclohexanol by the method of Heuckel and Heyder¹⁰⁸. The crude product was recrystallised from 80% ethanol.

Yield 64% as white plates. m.p. 47.5 - 48.5°C.

Literature m.p.¹⁰⁸ 47.8 - 48.7°C.

4-tert-butylcyclohexanonethiohemiketals.

These were prepared by the method of Eliel et al.¹⁰⁹ The crude mixture of liquid and solid epimers was then filtered at a water pump. The solid epimer was recrystallised from petroleum ether and then chromatographed on alumina column (80g. Brockman grade II, neutral) and eluted with petroleum ether.

The liquid epimer was similarly chromatographed on an alumina column (100 g. Brockman grade I, neutral) and eluted with 10% benzene in petroleum ether. Further elution with 50% benzene-petroleum ether yielded a little solid epimer. Their infra red spectra showed both to be free from ketone starting material. While the N.M.R. spectrum of the crude mixture showed two clearly distinguishable sets of overlapping triplets the spectra of the purified epimers showed both to be essentially pure. Liquid epimer: triplets centred on 5.95 τ and 7.05 τ , Solid epimer: triplets centred on 5.91 τ and 6.99 τ ; both in chloroform.

Solid epimer: Yield 22%. m.p. 74-75°C. Literature value 74-75°C.¹⁰⁹

Liquid epimer: Yield 13%.

2,4,6-trimethyl-thiadioxane (monothioparaldehyde)

This was prepared by the method of Müller¹¹⁰ and the crude product recrystallised four times from absolute ethanol.

Yield 6%. m.p. 55°C. Literature m.p. 55°C.¹¹⁰

2,4,6-trimethyl-1,3,5-trithianes (trithioparaldehydes)

These were prepared by a modification of the method of Campaigne et al.¹¹¹

Freshly distilled acetaldehyde (20 ml., 16g.) in alcoholic 2N hydrochloric acid (40 ml. absolute ethanol plus 10 ml. concentrated hydrochloric acid) was treated with hydrogen sulphide for $2\frac{1}{2}$ hrs. at room temperature and then the milky white solution shaken for 40 hrs. Two recrystallisations from absolute ethanol removed mono- and di-thioparaldehydes yielding a product m.p. $80-85^{\circ}\text{C}$ corresponding to the eutectic α/β mixture.¹¹¹

Fractional crystallisation from n-hexane yielded two fractions, one m.p. $94-99^{\circ}\text{C}$ (3.40g.), the other m.p. $118-123^{\circ}\text{C}$ (0.73g.).

Two recrystallisations of the first fraction from n-hexane at room temperature gave the pure α -isomer, and three recrystallisations of the second fraction from n-hexane at -5°C gave the pure β -isomer.

α -2,4,6-trimethyl-1,3,5-trithiane: Yield 1.79g. (8%).

m.p. $100-100.5^{\circ}\text{C}$. Literature m.p. $100.5-101^{\circ}\text{C}$.¹¹¹

β -2,4,6-trimethyl-1,3,5-trithiane: Yield 0.52g. (2%).

m.p. $126-127^{\circ}\text{C}$. Literature value¹¹¹ $126-127^{\circ}\text{C}$.

Cupric perchlorate hexahydrate

This was prepared from cupric carbonate by the action of perchloric acid. The reaction mixture was filtered, evaporated to dryness and the residue recrystallised from 90% ethanol. The purified material was then kept over phosphorous pentoxide to give the hexahydrate.

Yield 60%. m.p. 82°C . Literature m.p. 82.3°C .¹¹²

(III) Results and Discussion

As mentioned briefly before (section 4 (II)(a)), on adding copper (II) halide to a solution of a sulphide reduction of the copper occurred slowly with consequent removal of the deep colour of the complexed species and decrease in the line widths of the N.M.R. signals. The rate of this 'fading' reaction varied from ligand to ligand, and, not unexpectedly was very rapid in strong sunlight where photolysis of the sulphide ligand was quite rapid and quite appreciable. Decomposition of copper (II) halide complexes with sulphur ligands with accompanying reduction of the copper (II) to copper (I) has also been reported for the copper complexes with 2,5-dithiahexane.¹¹³

In order to study this 'fading' phenomenon various copper (II) salts were added to solutions of diethyl sulphide and the line widths measured over fairly extended time limits. Various complex copper salts were synthesised in an effort to obtain a stable system. It was found that the bis-(tetramethylammonium)-tetrahalocuprates had to be abandoned due to their poor solubility and hence the bis-(tetra-n-butylammonium)-tetrahalocuprates were finally studied together with the simple cupric halides.

The results of this study are discussed in the following section and the mechanisms of complex formation and relaxation processes discussed in section 4(III)(b). The results of line broadening studies in a variety of sulphur compounds are then discussed in the immediately following section (4(III)(c)).

(a) Relative stability of copper (II) salts in solutions of sulphide ligands.

The most extensively studied ligand was diethyl sulphide, it being studied with added cupric halides and bis-(tetra-n-butylammonium)-tetrahalocuprates in order to find the most stable system. The cupric halides were added from stock solutions in methanol and the tetrahalocuprates from stock solutions in both methanol and chloroform, this being done to test whether any recognisable solvent effect was evident. The results obtained are given in the tables following and each table of results represent only one of a series of results obtained under the same conditions. In each case the reproducibility at any point in time was found to be within 3 c/s for different solutions.

Table 75. Neat Et₂S + 2% MeOH + 10⁻²M CuBr₂

Time from addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s^a}$	τ	$\frac{\Delta\nu}{1/2c/s}$
0	7.47	1.7 ^a	8.78	1.7	-	-
8 min. ^c	7.34	43 ^b	8.77	2.2	6.64	1.0
16 "	7.40	41				
28 "	7.39	37	8.77	2.1	6.64	1.0
36 "	7.42	35				
48 "	7.41	31	8.77	2.2	6.65	1.0
56 "	7.44	30				
68 "	7.43	29	8.77	1.9	6.65	1.0
76 "	7.47	28				

- (a) maximum width of individual multiplet peaks.
 (b) overall band width
 (c) solution reddish-brown coloured on addition

Table 76. Neat Et₂S + 2% MeOH + 10⁻²M CuCl₂

Time from addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s^a$	τ	$\Delta\nu 1/2c/s$
0	7.47	1.8 ^a	8.78	1.6	-	-
1 min ^c	7.26	47 ^b	8.76	2.6	6.63	1.0
6 "	7.27	43	8.76	2.6	6.64	0.9
11 "	7.27	41	8.77	2.5	6.64	1.0
16 "	7.27	41	8.76	2.5	6.64	1.1
21 "	7.27	40	8.76	2.5	6.64	1.0
26 "	7.29	39	8.77	2.4	6.64	1.0
31 "	7.29	39	8.77	2.5	6.64	1.0
36 "	7.30	38	8.78	2.3	6.64	1.0
41 "	7.30	36	8.77	2.2	6.63	1.0
46 "	7.31	36	8.77	2.5	6.65	1.0
61 "	7.33	35	8.77	2.2	6.65	1.0
66 "	7.33	35	8.78	2.3	6.65	1.0
26 hrs.	7.39	28	8.78	1.7	6.67	1.0
31 "	7.37	28	8.78	1.7	6.65	1.0

(a) maximum width of individual multiplet peaks. (b) overall band width. (c) solution dark green coloured on addition of copper.

Table 77. Neat Et₂S + 2% MeOH + 10⁻²M [nBu₄N]₂CuBr₄.

Time from addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s^a$	τ	$\Delta\nu 1/2c/s$
0	7.49	1.8 ^a	8.80	1.7	-	-
2 min ^c	7.41	45 ^b	8.77	3.4	6.64	1.0
7 "	7.41	44	8.78	3.4	6.68	1.2
12 "	7.41	43	8.78	3.4	6.67	1.0
17 "	7.41	44	8.78	3.4	6.67	1.0
22 "	7.42	43	8.78	3.4	6.66	1.0
27 "	7.42	43	8.78	3.4	6.67	1.0
32 "	7.41	43	8.77	3.4	6.66	1.0
37 "	7.41	41	8.77	3.4	6.67	1.3
42 "	7.42	43	8.79	3.4	6.66	1.1
47 "	7.44	42	8.79	3.4	6.68	1.0
157 "	7.44	40	8.80	3.0	6.68	1.0
162 "	7.44	40	8.79	3.2	6.68	1.0
29 hrs.	7.46	28	8.79	2.6	6.67	1.2

(a) maximum width of individual multiplet peaks
 (b) overall band width
 (c) solution reddish brown coloured on addition.

Table 78. Neat Et₂S + 2%MeOH + 10⁻²M[nBu₄N]₂CuCl₄

Time for addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}^a$	τ	$\Delta\nu_{1/2c/s}$
0 ^d	7.46	1.7 ^a	8.79	1.7		
2 ^d min.	7.38	23 ^b	8.78	1.8	6.62	1.2
7 "	7.40	22				
12 "	7.41	22	8.78	1.8	6.63	1.1
17 "	7.41	22				
22 "	7.40	22	8.77	1.7	6.63	1.2
27 "	7.41	21				
32 "	7.41	22	8.78	1.7	6.63	1.1
37 "	7.42	21				
4 ¹ / ₄ hrs.	7.42	21 ^c	8.78	1.8	6.63	1.2
23 ² / ₃ "	7.41	16	8.78	2.1	6.63	1.1
29 ³ / ₄ "	7.41	15	8.77	1.8	6.62	1.3
4 days	7.42	13	8.78	1.9	6.63	1.1

- (a) maximum width of individual multiplet peaks.
 (b) total band width - peak showing some centre splitting.
 (c) total band width - peak showing clear centre splitting.
 (d) solution golden yellow coloured on addition.

From the results given in tables 75 to 78 it can be seen that the cupric halides appear to be more effective in broadening the methylene resonance in diethyl sulphide than are the tetrahalocuprates although the situation for the bromo compounds is not very clear due to rapid 'fading'. The tetrabromocuprate is more effective than the tetrachlorocuprate, and taking into consideration the fact that cupric bromide fades faster than cupric chloride as evidenced by the relative decay in line width, cupric bromide is probably more effective initially than cupric chloride. In general the bis-(tetra-n-butylammonium)-tetrahalocuprates are more stable than the corresponding simple cupric halides.

One of the most interesting results obtained for these solutions

is that whereas the solution containing tetrachlorocuprate was a golden yellow colour that containing cupric chloride was very dark green coloured; both bromo solutions were however brownish-red coloured. Thus it would appear that in neat diethyl sulphide solution there is a difference in complexed copper forms for the two chloro salts while both bromo salts may give rise to similar types of copper complexes. However, as can be seen from the results given later for one molar solutions of diethyl sulphide in chloroform, at lower copper concentrations both cupric chloride and tetrachlorocuprate give rise to green coloured solutions. This would appear to indicate that in neat solution the golden yellow colour probably arises from the tetrachlorocuprate ion which contains copper that is not complexed with the ligand. This point will be returned to in the discussion of the complex type (section 4(IV)) but it may be noted here that, as shown later in the general discussion, whenever poor complexing with tetrachlorocuprate occurs as evidenced by a poor degree of line broadening, the solution has a golden yellow colour.

It is interesting that the methanol CH_3 peak is not broadened, indicating preferential complexing of the copper with the sulphide ligand. In general, when sulphide complexing occurred the methanol peak was found to be sharp, but where little complexing occurred it was found to be very broad. Thus the width of the methanol peak gives an indication of the extent of sulphide complexing by the copper.

Table 79. 1M Et₂S in chloroform + 1% MeOH + 5.1 x 10⁻⁴M CuBr₂

Time after addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s^a$	τ	$\Delta\nu 1/2c/s$
0	7.43	1.7 ^a	8.74	1.7	-	-
3 mins ^c	7.42	34 ^b	8.73	1.7	6.51	1.2
9 "	7.43	29	8.74	1.7		
14 "	7.42	28	8.73	2.1	6.52	1.0
19 "	7.41	28	8.72	1.7		
24 "	7.42	28	8.73	1.7	6.52	1.0
29 "	7.43	27	8.73	2.1		
43½ hrs.	7.39	24 ^d	8.73	2.1	6.49	1.0

- (a) maximum widths of individual multiplet peaks.
 (b) overall band width.
 (c) solution reddish-brown coloured on addition.
 (d) peak now showing some centre splitting and outer multiplet members as slight shoulders.

Table 80. 1M Et₂S in CHCl₃ + 0.4% MeOH + 2.0 x 10⁻⁴M CuCl₂

Time after addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu 1/2c/s$	τ	$\Delta\nu 1/2c/s^a$	τ	$\Delta\nu 1/2c/s$
0	7.38	1.8 ^a	8.72	1.8	-	-
3 min. ^c	7.41	35 ^b	8.73	2.1	6.46	1.9
8 "	7.41	34	8.73	2.1	6.48	1.6
13 "	7.41	32	8.72	2.0	6.48	1.6
17 "	7.41	31	8.73	2.2	6.49	1.6
21 "	7.41	30	8.72	1.9	6.49	1.5
25 "	7.41	29	8.72	1.7	6.49	1.4
29 "	7.42	30	8.72	1.9	6.48	0.9
33 "	7.41	29	8.72	1.7	6.48	1.2
37 "	7.41	28	8.73	1.9	6.49	0.9
41 "	7.41	28	8.73	2.0	6.50	1.6
18 hrs.	7.40	29	8.71	1.7	6.47	1.1

- (a) maximum width of individual multiplet peaks
 (b) overall band width
 (c) solution dark green coloured on addition.

Table 81. 1M Et₂S in chloroform + 5.3×10^{-4} M [nBu₄N]₂CuBr₄

Time after addition	CH ₂		CH ₃	
	τ	$\Delta V_{1/2c/s}$	τ	$\Delta V_{1/2c/s}^a$
0	7.42	1.7 ^a	8.73	1.7
14 min. ^c	7.41	40 ^b	8.73	2.2
20 "	7.42	39	8.74	2.4
25 "	7.42	38	8.73	2.4
31 "	7.44	37	8.74	2.5
36 "	7.41	38	8.73	2.6
41 "	7.41	37	8.73	2.6
46 "	7.42	37	8.73	1.9
51 "	7.41	37	8.73	1.9
25 hrs.	7.43	27	8.74	1.8

(a) maximum width of individual multiplet peaks.

(b) overall band width.

(c) solution pale reddish brown coloured on addition.

Table 82. 1M Et₂S in chloroform + 4.2×10^{-4} M [nBu₄N]₂CuCl₄

Time after addition	CH ₂		CH ₃	
	τ	$\Delta V_{1/2c/s}$	τ	$\Delta V_{1/2c/s}^a$
0	7.35	2.3 ^a	8.72	1.9
3 min. ^c	7.35	46 ^b	8.73	2.7
9 "	7.38	47	8.72	2.9
15 "	7.37	46	8.72	2.6
20 "	7.37	46	8.72	2.6
25 "	7.38	46	8.73	2.6
31 "	7.37	45	8.72	2.6
37 "	7.37	45	8.72	2.5
42 "	7.37	45	8.72	2.5
47 "	7.37	44	8.72	2.6
52 "	7.37	44	8.72	2.6
21½ hrs.	7.37	34	8.72	2.1
45 "	7.38	28	8.73	2.0

(a) maximum width of individual multiplet peaks.

(b) overall band width.

(c) solution green coloured on addition.

Table 83. 1M Et₂S in chloroform + 0.4% MeOH + $4.0 \times 10^{-4}M$
[nBu₄N]₂CuCl₄

Time after addition	CH ₂		CH ₃		CH ₃ OH	
	τ	$\Delta\nu_{1/2c/s}$	τ	$\Delta\nu_{1/2c/s}^a$	τ	$\Delta\nu_{1/2c/s}$
0	7.42	2.0 ^a	8.73	1.7	-	-
10 min. ^c	7.35	47 ^b	8.72	2.5	6.47	4.5
14 "	7.37	46	8.71	2.6	6.46	4.3
19 "	7.35	45	8.71	2.6	6.47	3.3
24 "	7.36	43	8.71	2.5	6.47	1.9
29 "	7.36	43	8.71	2.5	6.47	1.7
34 "	7.35	43	8.71	2.6	6.47	1.6
39 "	7.35	43	8.71	2.5	6.47	1.2
44 "	7.36	43	8.72	2.5	6.49	1.0
48 "	7.35	42	8.71	2.5	6.48	1.1
19 hrs.	7.40	30	8.73	1.9	6.48	0.9
43 hrs.	7.42	24	8.74	1.8	6.52	1.0

(a) maximum width of individual multiplet peaks

(b) overall band width

(c) solution green coloured on addition.

From the results given in tables 79 to 83 for a one molar solution of diethyl sulphide it can be seen that the bromo copper salts appear to be less effective in broadening the line width than the corresponding chloro salts (in contrast to the situation with neat ethyl sulphide), but this could be due to the fact that the bromo species is less stable than the chloro species and that much of the copper (II) is removed by reduction in the first few minutes after addition. The solutions containing tetrahalocuprate salts are more stable than those with simple cupric halides.

Considering the solutions containing tetrachlorocuprate it can be seen that the presence of methanol makes no real difference to the overall band width of the methylene multiplet, and so the presence of methanol appears to have no effect on the formation of

the complex. The interesting result that with the tetrachlorocuprate solution the methanol line width decreases with time will be discussed in the following section on the type of complex formed in these solutions.

(b) Relaxation and complex formation mechanisms

As mentioned previously, copper (II) does not form isolable complexes with alkyl thio ethers unless chelate formation can occur. The production of a very dark green colour when cupric chloride was added to solutions of thio ethers indicate however that some complex formation occurs in solution. Addition of cupric perchlorate however was found to give no colour and the N.M.R. spectrum of the ligand appeared unaffected, but subsequent addition of lithium chloride produced a green or yellow green colour and the N.M.R. spectrum now showed selective broadening indicating that complex formation was now occurring. The extent of line broadening was found to increase with increasing chloride condition as shown in Table 84. Both salts were added from stock solutions in methanol and the line widths given are the average of two scans of the spectrum obtained immediately after addition of lithium chloride (within less than ten minutes).

Table 84. Effect of added LiCl on 1MET₂S in chloroform containing Cu(ClO₄)₂

Conc. MeOH%	Conc. Cu (ClO ₄) ₂ <u>M</u>	Conc. LiCl <u>M</u>	CH ₂ τ	ΔV 1/2c/s	CH ₃ τ	ΔV 1/2c/s ^a	CH ₃ OH τ	ΔV 1/2c/s
2.5	10 ⁻²	2.5 x 10 ⁻³	7.49	2.9 ^a	8.80	1.7	6.68	1.0
3	10 ⁻²	5 x 10 ⁻³	7.45	15 ^b	8.79	1.7	6.68	1.0
3	10 ⁻²	10 ⁻²	7.26	45 ^c	8.78	2.9	6.65	1.0
4	10 ⁻²	2 x 10 ⁻²	7.27	44 ^c	8.79	1.7	6.66	1.0

(a) maximum width of individual multiplet peaks

(b) very broad quartet, the outer members showing as shoulders.
Width taken at half highest peak height.

(c) overall band width.

Thus the species that complexes with the sulphide ligand must be a chloro copper species. This is confirmed by the fact that in aqueous solution cupric chloride gives very little selective broadening of the SCH₂ resonance of thiodiglycol, whereas as excess chloride ion was added the SCH₂ resonance began to broaden more than the OCH₂ resonance as shown in Table 85. The results in the table are the average of two scans of the spectrum obtained immediately after addition of cupric chloride to a solution of both ligand and chloride. The internal reference standard was tert-butanol.

Table 85. 1M Thiodiglycol ($\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$) in D_2O +
KCl + CuCl_2 .

Conc. CuCl_2 M	Conc. KCl M	τ	DOH $\Delta\nu$ $\frac{1}{2} \text{ c/s}$	τ	OCH_2 $\Delta\nu$ $\frac{1}{2} \text{ c/s}$	τ	SCH_2 $\Delta\nu$ $\frac{1}{2} \text{ c/s}$	tert- butyl $\Delta\nu$ $\frac{1}{2} \text{ c/s}$	Colour of solution
10^{-3}	-	5.30	1.5	6.24	16^a	7.21	19	0.9	very pale blue
10^{-3}	0.26	5.32	1.5	6.24	15^a	7.22	21	0.9	very pale blue
10^{-3}	0.50	5.36	1.3	6.25	4.6^b	7.22	22	0.9	very pale blue- green
10^{-3}	1.02	5.40	1.1	6.24	4.1^b	7.21	25	0.9	very pale yellow green
10^{-3}	2.00	5.48	1.4	6.25	5.2^b	7.20	34	0.9	pale yellow green

- (a) peak just showing outer triplet members as shoulders - overall band width measured.
 (b) peak showing clear triplet splitting - half width of centre component measured.
 (c) overall band width.

The decrease in the OCH_2 line width and the increase in the SCH_2 width as the chloride concentration indicates a change from a possible bi- or tridentate chelate, bonded through both sulphur and hydroxyl to a preferred sulphur bonded complex as the proportion of chloro copper species increases. This is borne out by the change in the colour of the solution from pale blue to yellow-green, the latter being the colour of a similar chloroform solution containing about one-fourth the concentration of copper.

Thus the species which complexes with thio ether ligands is a chloro copper species. The increase in the amount of the sulphur bonded species in aqueous solution as the chloride concentration is increased is shown by changes in the U.V. spectra of the solutions

as shown in Table 86. All U.V. spectra were obtained on a Perkin-Elmer 137 U.V. spectrometer using 1 cm. cells with the appropriate solvent as blanks. All spectra were obtained immediately after adding the appropriate copper salt.

Table 86. Aqueous Copper (II) solutions - U.V. spectra.

Conc. $\text{Cu}(\text{ClO}_4)_2$ <u>M</u>	Conc. KCl <u>M</u>	Thiodiglycol	λ max. (m μ).
10^{-2}	-	absent	ca 200
"	0.25	"	ca 250
"	0.5	"	ca 250
"	1.0	"	250 (O.D. about 0.8)
"	2.0	"	252 (O.D. > 1.5)
"	3.0	"	254 (O.D. >> 1.5)
10^{-2}	-	present (1M)	ca 250
"	0.25	"	ca 255; ca 330-340
"	0.5	"	ca 255; ca 335-340
"	1.0	"	ca 260; 340
"	2.0	"	ca 275; 345

The first three results shown in the table for the solutions which did not contain thiodiglycol represent only the wavelength at which the solutions became transparent, but the latter three are true absorption peaks. The values of λ max. for the latter two solutions were obtained by offsetting the base line of the spectrometer. In the case of the solutions containing thiodiglycol the 250 - 275 m μ figures similarly represent the wave-length at which the solutions had an optical density of greater than 1.5, but the longer wave length figures represent the measured values of definite

absorption maxima. Unfortunately no real value of optical density could be obtained as these absorption peaks were superimposed on the shoulder of the more intense absorption. However, the optical density of these peaks clearly increased with increasing chloride concentration, as did the resolution of the absorption maximum. Similarly, as the chloride concentration increased so too did the intensity of the colour of the solutions, changing from yellow-green to a quite intense green colour.

Thus the absorption in the region 330-345 m μ must be due to the complexed sulphur species since no such absorption occurs in the absence of the ligand. Somewhat similar behaviour is shown in chloroform solution inasmuch as new absorption peaks were obtained when sulphide ligands were present, although at different wavelengths from those in aqueous solution. In the chloroform solutions absorption peaks were also obtained in the visible region of the spectrum as shown in table 87. Again no accurate estimate of the optical densities at the various wavelengths could be obtained as the absorption peaks tended to overlap and were either relatively very weak or very strong. However in the table the relative intensities are given in parenthesis, ranging from very weak (v.w.) through medium (m) to very strong (v.s.).

Table 87. Chloroform copper (II) solutions - U.V. spectra

Conc. CuCl_2 <u>M</u>	Conc. $[\text{nBu}_4\text{N}]_2\text{CuCl}_4$ <u>M</u>	Et_2S	Benzyl Sulphide	$\lambda_{\text{max.}}$ (m μ).
2.5×10^{-4}	-	-	-	295 (w)
2.5×10^{-4}	-	1M	-	ca 260(v.s.), 452 (w)

(Table 87 Contd. P.158)

Table 87 (Contd.)

Conc. CuCl_2 <u>M</u>	Conc. $[\text{nBu}_4\text{N}]_2$ CuCl_4 <u>M</u>	Et_2S	Benzyl Sulphide	λ max. (m μ).
-	4.1×10^{-4}	-	-	300 (v.w.), ca 475(v.w)
-	1.5×10^{-3}	-	-	300 (m), 472(v.w)
-	4.1×10^{-4}	1M	-	ca 260 (v.s.), ca 310-320 (v.w.), 452(m)
2.5×10^{-4}	-	-	1M	ca 270 (v.s.)
-	1.5×10^{-3}	-	1M	ca 270 (v.s.), 445 (m)

The absorption peak at about 450 m μ may be assigned to the sulphide complex since with cupric chloride it only appears when diethyl sulphide is added. The presence of this peak in the solution containing both tetrachlorocuprate and diethyl sulphide would suggest that both copper species give rise to the same type of complex. The peak at about 470 m μ may be assigned to the normal tetrahalocuprate species since it is not shown by any of the solutions containing cupric chloride. The absence of this peak in the diethyl sulphide solution containing tetrachlorocuprate is probably due to that when complex formation occurs the concentration of free tetrachlorocuprate is so reduced as to render the initially weak absorption undetectable at the concentrations used, the same probably being true of the solution containing benzyl sulphide.

While the complexed species appear to be of the same type for both copper salts the fact that the tetrahalocuprates are less effective in producing line broadening than are the corresponding simple halides suggests that the extent of complexing is dependent on the nature of the copper salt employed. The most obvious difference between the two types of salts is in the number of halide

ions in the molecule, and one possible explanation for the difference in effectiveness could be that the complexed species is one containing less than four halide ions. Thus in the tetrahalocuprate solutions an equilibrium would be set up in which the sulphide ligand displaces halide ion to give the complexed species.

If such an equilibrium does in fact exist in solution then the extent of line broadening will be dependent on the total halide concentration. In order to test whether an equilibrium of this type exists the effect of added tetra-*n*-butylammonium bromide on the line broadening in diethyl sulphide produced by tetrabromocuprate was studied with the results shown in table 88.

Table 88. 1M Et₂S in CHCl₃ + [nBu₄N]₂CuBr₄ + nBu₄NBr

Conc. [nBu ₄ N] ₂ CuBr ₄ <u>M</u>	Conc. nBu ₄ NBr <u>M</u>	Time after addition min.	τ	CH ₂	CH ₃	
				ΔV 1/2c/s ^a	ΔV 1/2c/s ^b	
5.3 x 10 ⁻⁴	nil	14	7.41	40	8.73	2.6
		20	7.42	39	8.73	2.8
		25	7.42	38	8.74	2.8
		51	7.41	37	8.73	2.2
5.3 x 10 ⁻⁴	1.2 x 10 ⁻³	14	7.43	37	8.75	2.6
		19	7.41	34	8.74	2.6
		24	7.42	34	8.74	2.6
		51	7.42	33	8.74	2.8
5.3 x 10 ⁻⁴	1.4 x 10 ⁻²	13	7.41	27	8.74	3.1
		18	7.40	26	8.74	2.9
		22	7.44	25	8.74	2.9
		52	7.43	25	8.74	3.0

(a) overall band width.

(b) maximum width of individual multiplet peaks.

The decrease in line width of the methylene multiplet as the concentration of excess halide increases would thus tend to confirm

that such an equilibrium does in fact exist. Thus the complexed species are probably the same for both the simple halides and the tetrahalocuprates, having less than four halide ions co-ordinated to the copper ion. The extra stability of the tetrahalocuprates towards 'fading' can then be explained on the basis of the equilibrium between the tetrahalocuprate and the complex, the former acting as a copper reservoir. Thus as copper (II) is removed by reduction the concentration of tetrahalocuprate would change to maintain the equilibrium, so giving a relatively stable line width until such time as the cupric copper content becomes seriously depleted when reduction in line width occurs.

This equilibrium mechanism could also explain the reduction in the line width of the methyl group of the added methanol shown in table 83. If the methanol is co-ordinated to the tetrahalocuprate it would be in a paramagnetic environment and so would be broadened, but as the tetrachlorocuprate breaks down to replenish the copper removed by reduction the methanol would then return to the bulk diamagnetic environment and so the line width would decrease as in fact occurs.

In aqueous solution, in the absence of added halide the copper will be in the hexa-aquated form but as chloride ion is added a somewhat similar competition equilibrium would be set up between the aquated and the complexed chloro species. In this case however as the chloride concentration is increased the proportion of the complexed chloro copper species would increase and not decrease. In fact this behaviour is shown in practice as can be seen from table 85.

The existence of a competitive equilibrium in the case of the tetrahalocuprate in which the sulphide ligand and chloride ion compete for the copper would mean that the relative effectiveness of the tetrahalocuprate in producing line broadening as compared to the simple halides would depend on the following three factors.

- 1) the concentration of added halide,
- 2) the concentration of sulphide, and
- 3) the nature of the sulphide present.

The first of these factors has already been considered, and the third will be discussed later with respect to the various ligands studied. The effect of ligand concentration on the relative effectiveness in producing line broadening of cupric chloride and tetrachlorocuprate has been studied in the case of diethyl sulphide with the results shown in table 89. The respective concentrations of cupric chloride and tetrachlorocuprate used were deliberately chosen to give approximately equal line widths with one molar diethyl sulphide in order to facilitate comparison at the other ligand concentrations.

Table 89.

Conc. Et ₂ S <u>M</u>	Conc. CuCl ₂ <u>M</u>	Conc. [nBu ₄ N] ₂ CuCl ₄ <u>M</u>	Time after addition (mins.)	τ	CH ₂ $\Delta\nu$ 1/2c/s	CH ₃ τ	$\Delta\nu$ 1/2c/s
0.5	2.6 x 10 ⁻⁴	-	11	ca7.5	>120	8.73	2.6
			45	ca7.5	>120	8.73	2.7
0.5	-	4.1 x 10 ⁻⁴	12	7.40	55	8.74	2.8
			33	7.38	55	8.73	2.6
1	2.5 x 10 ⁻⁴	-	10	7.42	43	8.74	2.6
			49	7.41	38	8.74	2.4

(Contd. P.162)

Table 89 (Contd.)

Conc. Et ₂ S <u>M</u>	Conc. CuCl ₂ <u>M</u>	Conc. [nBu ₄ N] ₂ CuCl ₄ <u>M</u>	Time after addition (mins.)	τ	CH ₂ ΔV 1/2c/s	CH ₃ τ	ΔV 1/2c/s
1	-	4.0 x 10 ⁻⁴	12	7.39	46	8.73	2.6
			42	7.38	42	8.72	2.5
2	2.6 x 10 ⁻⁴	-	10	7.45	28	8.75	1.7
			43	7.43	24	8.75	1.8
2	-	4.1 x 10 ⁻⁴	9	7.43	29	8.75	1.9
			35	7.43	27	8.74	1.7

Whilst at 1M and 2M diethyl sulphide concentration the two copper salts give similar line widths at the respective concentrations employed, at 0.5M ligand concentration the cupric chloride is more effective by far. Thus as the ligand concentration decreases the competition by halide ion becomes of greater importance in the case of tetrachlorocuprate, and the equilibrium between the complexed copper and the tetrachlorocuprate is displaced towards the latter. Thus both ligand and halide ion concentration are of importance in determining the effectiveness of the tetrachlorocuprate relative to cupric chloride.

In order to render meaningful comparison possible the ligand concentration was kept constant at 1M in the study of the various sulphur ligands reported later, except where the availability of the compound did not permit this. In such cases the concentration used is given in the text and approximately the same concentration used for each copper addition.

Considering now the mechanism of the broadening of the peaks,

it is generally accepted ^{32,33} that ligand exchange in copper complexes is very fast and so the Swift and Connick equations for case A and case C cannot be operative (see section 1(V)). Copper (II) like manganese (II) has a long electron spin relaxation time, and so both τ_c and τ_e will be dominated by τ_h , the correlation time for chemical exchange. Thus T_{1M} will be given by equation (14) and will be dipolar determined, and T_{2M} by equation (15) and will be dominated by the scalar term.

That spin-spin coupling between the methylene and methyl protons is still shown in diethyl sulphide even when the methylene resonance is very broad indicates that for the methylene protons $T_1 \gg 1/J$ where J is the proton spin-spin coupling constant. Similar behaviour has been reported for the β -hydroxypropionate anion chelated with copper (II) ¹¹⁴ and in electron transfer reactions between alkylbenzenes and their anions ^{70c}.

From the results given in tables 75 to 83 it is clear that the line width is large compared to any shift, and so consideration of the relationship given by equation (27) thus rules out case B control for the observed line widths and shift. The operative mechanism must then be case D control, and so

$$\frac{1}{T_{2p}} = \frac{f}{T_{2M}} \quad \text{-----} \quad (25)$$

$$\Delta\omega = f\Delta\omega_M \quad \text{-----} \quad (26)$$

(c) Comparison of selective collapse in various sulphur ligands

A. Chloroform solutions.

Although cupric chloride exhibits relatively rapid 'fading' in solutions of sulphide ligands, especially if the compound undergoes decomposition fairly easily, both this compound and bis-(tetra-n-butylammonium)-tetrachlorocuprate (hereafter referred to as tetrachlorocuprate and indicated in the tables as $\text{CuCl}_4^{=}$) were studied since the colour, if any, produced by addition of the former indicated immediately whether complex formation occurred. Comparison of the relative molar concentrations of the two salts required to give similar line widths was found to be indicative of the degree of stability of the complex. Whereas cupric chloride complexes quite readily with any sulphide ligand the degree of complexing when tetrachlorocuprate is present depends on the relative degree of competition between sulphide and chloride.

In the following discussion the ligands are considered in groups, each group being composed of a similar ligand type, and the results are included in the text for ease of reference. In the cases where a solution of cupric chloride in methanol was added, if no line width for the methanol methyl resonance is given the line width was essentially unaffected. In such cases the copper is bound preferentially to the sulphide ligand. Where significant broadening of the methanol resonance occurred the line width is given.

The reported line widths for clearly resolved multiplets are the maximum values for the individual peaks in the multiplet. For broadened multiplets the overall band widths at half height is given.

It must be stated however that the relationship between the band width and the "true" line width cannot be obtained from the results given, as for a given "true" line width the band width is dependent on the number of peaks in the multiplet, their relative intensities and on the coupling constant separating the peaks in the multiplet. Thus for a multiplet containing many peaks with a small separation a relatively small degree of actual line broadening would lead to only an apparently broad single band to appear whereas with the same degree of broadening in say a triplet of wide separation an apparently only slightly broadened peak would be obtained showing clear splitting. It is for this reason that the relative concentrations of the two copper salts required to produce approximately the same overall band width with the same ligand are compared and not the widths produced by the same concentration of the salts.

Since the early work of Li⁴⁰ no systematic N.M.R. study has been reported in which the line broadening produced by Cu(II) has been used to determine structural differences in sulphur containing ligands. The results obtained in this study in chloroform solution are reported in two parts; firstly those obtained with relatively simple ligands which give simple N.M.R. spectra, and later those obtained with more complex ligands.

1. Simple ligands.

With diethyl- and di-n-propyl sulphide cupric chloride appears to be about 1.5 times as effective as tetrachlorocuprate in broadening the methylene group next to the sulphur atom, but is much less stable. The same is probably true for iso-amyl sulphide, but here both exhibit

rapid fading. An example of the selective broadening produced by tetrachlorocuprate in the case of diethyl sulphide is shown in figure 2.

Table 90.

Sulphide	Conc. CuCl_2 $\underline{\text{M}}$	Conc. CuCl_4^- $\underline{\text{M}}$	Time after addition (mins.)	τ	CH_2 ΔV $1/2c/s^b$	terminal CH_3 ΔV $1/2c/s^a$	τ
diethyl sulphide	Nil	Nil	-	7.39	1.8 ^a	8.73	1.7
	2.5×10^{-4}	-	5	7.34	44	8.74	1.9
			49	7.41	38	8.74	2.5
	4.1×10^{-4}	-	5	7.42	ca60	8.73	3.4
			40	7.41	ca55	8.74	2.5
	-	4.0×10^{-4}	8	7.37	46	8.72	2.5
			42	7.38	40	8.73	2.5
	-	6.0×10^{-4}	6	7.39	54	8.74	2.9
			85	7.39	43	8.75	2.6
di-n- propyl sulphide	-	-	-	7.48	2.6 ^a	9.01	2.6
	2.5×10^{-4}	-	5	7.48	41	9.01	2.7
			57	7.51	20	9.01	2.5
	4.0×10^{-4}	-	12	7.49	ca65	9.00	3.1
			40	7.44	ca60	9.03	2.6
	-	4.0×10^{-4}	6	7.46	40	9.01	3.4
			97	7.47	38	9.01	2.6
	-	6.0×10^{-4}	12	7.45	52	9.01	2.8
			79	7.41	48	9.01	2.7
di-iso- amyl sulphide	-	-	-	7.47	2.6 ^a	9.09	1.7
	2.5×10^{-4}	-	5	7.47	18 ^c	9.09	1.7
			10	7.48	12 ^c	9.10	1.7
	4.1×10^{-4}	-	5	7.50	27	9.10	1.7
			23	7.47	19	9.07	1.7
	-	4.1×10^{-4}	5	7.48	19	9.10	1.7
			37	7.47	5.2 ^d	9.09	1.7

(Contd. P.167)

Table 90 (Contd.)

Sulphide	Conc. CuCl_2 $\underline{\text{M}}$	Conc. = CuCl_4 $\underline{\text{M}}$	Time after addition (mins.)	CH_2		terminal CH_3	
				τ	$\Delta\nu$ $1/2c/s^b$	τ	$\Delta\nu$ $1/2c/s^a$
di-iso- amyl sulphide	-	6.1×10^{-4}	5	7.50	27	9.11	1.7
			21	7.50	20	9.09	1.7

- (a) maximum width of individual multiplet peaks
 (b) overall band width
 (c) peak showing clear triplet splitting - width the overall band width at half centre peak height.
 (d) width of centre peak of triplet.

Thus for normal alkyl sulphide ligands cupric chloride and tetrachlorocuprate are of similar effectiveness in producing line broadening, the ratio of their effectiveness being between 1.5 and 2 when the ligand concentration is 1M .

With rather hindered sulphides, or those having a smaller degree of electron availability on the sulphur atom, this ratio becomes much larger, ranging from about 6 with benzyl sulphide to about 35 in the case of thioanisole. With iso-propyl sulphide the overall behaviour is similar to that with benzyl sulphide although accurate measurement of the line width of the CH peak was difficult due both to the complexity of the multiplet and that rapid 'fading' occurred.

Table 91.

Sulphide	Conc. CuCl_2 $\underline{\text{M}}$	Conc. = CuCl_4 $\underline{\text{M}}$	Time from addition (mins.)	τ	CHn		terminal CH_3		C_6H_5	
					$\Delta\nu$ $1/2c/s$	τ	$\Delta\nu$ $1/2c/s$	τ	$\Delta\nu$ $1/2c/s$	τ
di-iso- propyl sulphide	2.6×10^{-4}	-	-	7.01	2.0	8.74	1.0			
			5	7.00	18^a	8.75	1.4			
			21	7.01	2.6^b	8.74	1.7			

(Contd. P.168)

Table 91 (Contd.)

Sulphide	Conc. CuCl_2 M	Conc. = CuCl_4 M	Time from addition (mins.)	CHn		terminal CH_3		C_6H_5	
				τ	$\frac{\Delta\nu}{1/2\text{c/s}}$	τ	$\frac{\Delta\nu}{1/2\text{c/s}}$	τ	$\frac{\Delta\nu}{1/2\text{c/s}}$
di-iso- propyl sulphide	4.2×10^{-4}	-	6	6.99	30	8.74	1.6		
			32	7.00	20 ^a	8.74	1.1		
	-	6.2×10^{-4}	4	6.98	5.1 ^c	8.74	1.1		
			38	6.98	5.1 ^c	8.74	1.3		
	-	1.6×10^{-3}	5	6.93	23	8.76	1.2 ^a		
			26	6.95	19	8.74	1.3 ^a		
benzyl sulphide	-	-	-	6.47	1.6			2.77	1.7
	2.6×10^{-4}	-	5	6.42	55			2.76	1.7
			32	6.44	43			2.78	1.7
	4.1×10^{-4}	-	10	6.41	ca 95			2.75	1.7
			38	6.45	78			2.76	1.7
	-	1.0×10^{-3}	5	6.38	29			2.78	1.7
			65	6.39	27			2.77	1.7
	-	2.0×10^{-3}	6	6.34	36			2.77	1.7
			51	6.34	35			2.77	1.7
	-	-	-	7.55	1.2			2.8 ^d	
thio- anisole	2.6×10^{-3e}	-	4	7.52	15			2.8	
			29	7.52	11			2.8	
	1.0×10^{-3f}	-	5	7.49	27			2.8	
			30	7.46	27			2.8	
	-	1.1×10^{-3g}	3	7.53	1.7			2.8	
			5	7.53	1.7			2.8	
	-	2.1×10^{-3g}	3	7.51	2.3			2.8	
			6	7.51	2.4			2.8	

- (a) peak just showing signs of multiplet splitting - width that at half highest peak height. (c) centre peak width
 (b) single peak width (d) peak almost completely masked by chloroform resonance
 (e) solution pink coloured. 0.5% methanol added, its line width initially 3.6 c/s fading to 2.6 c/s.
 (f) solution reddish-brown coloured. 2% methanol added, its line width 10 c/s steady with time. (g) solution golden yellow coloured

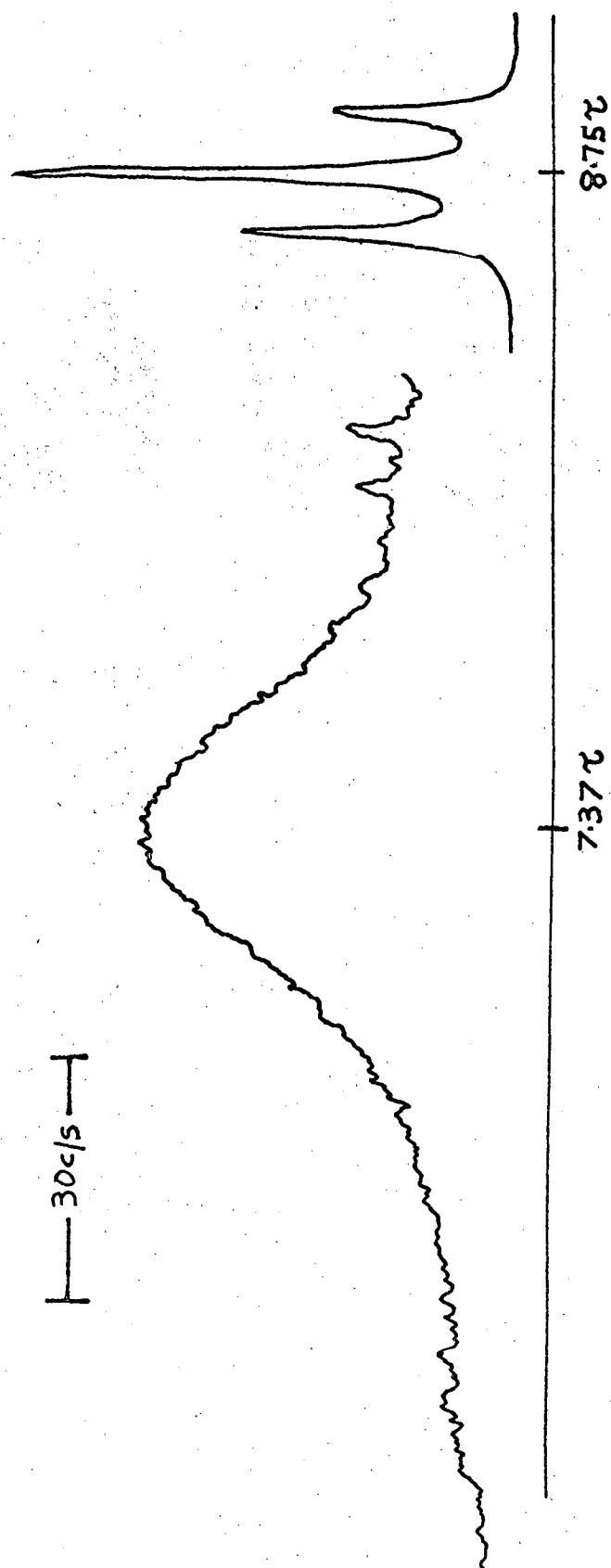


Fig. 2. 1M diethyl sulphide in chloroform + 4.0×10^{-4} M tetrachlorocuprate

From the results in table 91 it can be seen that as the degree of steric hindrance and of electron withdrawal from the sulphur atom increases so too does the relative effectiveness of the cupric chloride as compared with the tetrachlorocuprate. Thus this system of relative effectiveness would enable the stability of the copper complex of a sulphide of unknown structure to be evaluated relative to those of known structure. As shown it enables a distinction to be made between benzyl sulphide and thioanisole in which the electron withdrawal by the phenyl ring increases as the intervening CH_2 group is removed.

The results obtained for thioanisole are very interesting in many ways; the reddish brown colour produced on adding cupric chloride indicates that a different complex is formed than with benzyl sulphide or indeed any of the previous sulphides which gave the 'usual' green colour, and the large ratio of the effectiveness of the two salts indicates the great dependence of the degree of complexing in the case of the tetrachlorocuprate on ligand stereochemistry and on electron withdrawing tendency. The fact that with cupric chloride in going from one solution to the other the increase in line width is less than the proportionate increase in the copper concentration is rather puzzling, especially as with benzyl sulphide the line width increases by approximately the same factor as the copper concentration increase. This apparent discrepancy may be due to the two ligands forming different types of complexes as indicated by the different colours of the solutions, and perhaps also to more effective competition by methanol in the case of thio-

anisole. Thus while the ratio of the concentrations of methanol and copper is the same in both thioanisole solutions the line width of the methanol peak increased by a factor of three in going from one to the other.

It is interesting that for benzyl sulphide the line width is less than doubled when the concentration of tetrachlorocuprate is doubled, although for cupric chloride the two are proportional. This must also be due to the fact that the formation of the complex involves displacement of chloride from the tetrachlorocuprate; at the higher chlorocuprate concentration the concentration of chloride will also be higher and hence the extent of complexing is less than might be expected.

Whilst the monosulphides complex to varying degrees, depending on the degree of hindrance and the electron availability, showing marked selective broadening of the protons α to the sulphur as compared to those further removed, the disulphides show no signs of any significant degree of complexing. Line broadening was also not observed with ethylthiocyanate or thiophen. In all of these cases, when diethyl sulphide was added and the spectra re-run a new triplet corresponding to the methyl group of the diethyl sulphide appeared but no diethylsulphide methylene peak was observed. This, together with the fact that immediately after addition of the diethyl sulphide the solutions became very dark green coloured showed that the copper had not been reduced by impurities and that in fact complex formation did not occur with these ligands. This was also confirmed by the fact that the methanol peak was so broad as to be virtually indistinguishable in the absence of added diethyl sulphide. The results

obtained with the disulphides and ethylthiocyanate are shown in table 92, only cupric chloride being added since this is more effective than tetrachlorocuprate.

Table 92.

Ligand	Conc. CuCl_2 <u>M</u>	Time after addition (mins.)	τ	CH_2	τ	CH_3	τ	CH_2OH
				$\Delta\nu$ 1/2c/s		$\Delta\nu$ 1/2c/s		$\Delta\nu$ 1/2c/s
diethyl disulphide	1.0×10^{-2}	0	7.28	2.2	8.67	1.7	6.50	6.0
		3 ^a	7.25	3.8	8.67	1.8	a	
		>6 ^b	7.29	2.2	8.68	c	6.53	2.2
di-n- propyl disulphide	1.0×10^{-2}	0	7.31	2.2	9.00	2.6	6.49	2.5
		6 ^a	7.29	5.1	9.01	2.8	a	
		>10 ^b	7.31	2.6	9.01	2.6	6.52	2.6
ethyl thio- cyanate	1.0×10^{-2}	0	7.00	1.8	8.48	1.7	6.58	4.2
		3 ^a	6.98	2.6	8.46	2.2	a	
		>8 ^b	6.98	2.2	8.47	1.7	6.53	2.6

- (a) methanol peak broadened into base line
 (b) after addition of about 10% diethyl sulphide
 (c) overlapping with very broad methyl peak of added diethyl sulphide.

That no line broadening is shown by the disulphides is not surprising in view of the well known fact that compounds containing the -S-S- linkage do not in general form complexes.⁹⁸ Similarly the fact that thiophen does not complex is in accord with the fact that aromatic sulphides do not form complexes.⁹⁸ While thiocyanate ion is a strong complexing species bonding usually occurs through the nitrogen atom^{97b} and so if complexing does occur with ethylthiocyanate unpaired electron spin density would be unlikely to reach the ethyl group to any significant extent as this would require transfer over three bonds and so little line broadening would be expected as is the

case in practice.

While thiophen showed no real line broadening (the complexity of the A_2B_2 spectrum rendering accurate measurement of line widths impossible although very little loss of resolution was observed on adding copper), tetrahydrothiophen showed significant line broadening on adding copper. Similarly 1,4 thioxane and 1,4 dithiane showed extensive line broadening but 1,4 dioxane gave no real line broadening as shown in table 93.

Table 93.

Ligand	Conc. $CuCl_2$ \underline{M}	Conc. $CuCl_2$ \underline{M}	Time after addition (mins)	$\alpha-CH_2^a$		$\beta-CH_2$	
				τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$
tetra- hydro thiophen	-	-	-	7.16	1.6 ^b	8.06	1.7 ^b
	2.5x10 ⁻⁴	-	5 40	7.14 7.14	49 14	8.06 8.06	c 1.7
	4.1x10 ⁻⁴	-	5 23	7.14 7.14	48 17	8.06 8.06	c 1.8
	-	4.1x10 ⁻⁴	5 23	7.14 7.14	43 19	8.06 8.06	c 2.1
	-	6.1x10 ⁻⁴	5 22	7.08 7.12	56 39	8.06 8.06	c c
	-	-	-	7.11	0.9		
1,4-di- thiane	2.6x10 ^{-4a}	-	5 36	7.10 7.10	6.6 2.1		
	4.1x10 ^{-3a}	-	5 20	7.10 7.10	14 10		
	-	4.2x10 ⁻⁴	5 30	7.08 7.08	10 10		
	-	6.2x10 ⁻⁴	5 37	7.06 7.08	18 15		
	-	-	-	7.11	0.9		
	-	-	-	7.11	0.9		

(Contd. P.174)

Table 93 (Contd.)

Ligand	Conc. CuCl_2 $\underline{\text{M}}$	Conc. CuCl_4 $\underline{\text{M}}$	Time after addition (mins.)	CH_2^a τ	$\Delta\nu$ $1/2\text{c/s}$	CH_2 τ	$\Delta\nu$ $1/2\text{c/s}$
1,4-thio- xane	-	-	-	7.38	1.8	6.07	2.6
	2.5×10^{-4}	-	5	7.38	48	6.06	12^e
			25	7.32	47	6.05	12^e
	4.0×10^{-4}	-	5	7.28	>60	6.05	12^e
			56	7.26	<u>ca</u> 60	6.05	12^e
	-	4.0×10^{-4}	5	7.32	25	6.08	4.3^f
			44	7.32	23	6.07	4.1^f
	-	6.0×10^{-4}	5	7.30	30	6.05	11^e
			26	7.32	30	6.07	10^e
	-	-	-	6.32	0.9		
dioxan	2.6×10^{-4}	-	7	6.32	0.9		
	-	4.1×10^{-4}	5	6.32	0.9		

- (a) in thio compounds SCH_2 , in dioxan single peak resonance.
 (b) width of centre, most intense peak.
 (c) slightly broadened, showing 5 clear peaks but no accurate measurement possible.
 (d) solution brownish-yellow coloured on addition of copper rather than 'usual' green colour.
 (e) very broad triplet, width the overall width at half highest peak height.
 (f) width of centre peak of triplet.

The extensive selective collapse exhibited in tetrahydrothiophen as compared to thiophen shows that the lack of complex formation in the latter is due to its aromatic character and not to any steric hindrance. The very slight collapse shown by 1,4-dithiane as compared to tetrahydrothiophen however appears anomalous at first sight, but the colour of the solutions after addition of copper were different (tetrahydrothiophen being green whereas 1,4-

thioxane brownish-yellow coloured) indicating that different types of complexes are formed with the two ligands. It is known that 1,4-dithiane complexes are polymeric in the solid state^{97b} and it may be that in solution the complex is at least partially polymeric, hence explaining the difference in colour and degree of line broadening.

Comparison of the results obtained with 1,4-thioxane and dioxan indicates that copper (II) co-ordinates readily with sulphur but not with oxygen ethers. This preferential bonding to the sulphur in 1,4-thioxane is in accord with Walton's observations in his infra-red studies of 1,4-thioxane complexes.^{104b} However the OCH_2 resonance is somewhat broadened (though much less than the SCH_2 resonance) possibly suggesting that some degree of oxygen bonding does occur, perhaps to form polymeric or chelate structures. Although it is known that cupric chloride forms isolable solvates with dioxan¹¹⁵, the fact that no line broadening occurs in chloroform solution indicates that such oxygen bonding is very weak, certainly not strong enough to allow transfer of electron spin, and so the cupric chloride must be preferentially co-ordinated to the added methanol, and, with the tetrachlorocuprate, chloride ion co-ordination probably occurs rather than dioxan co-ordination. This is confirmed by the fact that in the case of cupric chloride addition the methanol peak was so broad as to be indistinguishable from the base line.

Thus in general thio ethers co-ordinate much more strongly with copper than oxygen ethers. As has already been shown in table 85,

for thiodiglycol in aqueous solution hydroxyl groups co-ordinate almost as strongly as thio ether linkages, and while in chloroform solution sulphur bonding is more strongly preferred, some hydroxyl bonding still occurs indicating that the hydroxyl group is a stronger donor than an etherial oxygen. Thus with thiodiglycol and 2-(methyl thio)-ethanol whilst the groups next to the sulphur atom were extensively broadened, some broadening of the group next to the hydroxyl group also occurred indicating that some degree of chelation occurred as well as mono-dentate complexing through sulphur. As would be expected, with 3,6-dithiaoctane strong chelate formation occurred as evidenced by the very extensive broadening of the complete spectrum.

Table 94.

Ligand	Conc. CuCl_2 $\underline{\text{M}}$	Conc. CuCl_2 $\underline{\text{M}}$	Time after addition (mins.)	OCH_2		SCH_2		SCH_3	
				τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s	τ	$\Delta\nu$ 1/2c/s
thiodi- glycol (1.3M)	-	-	-	6.20	a	7.25	2.2		
	4.1×10^{-4}	-	5	6.24	4.3	7.23	14		
			29	6.22	4.3	7.23	15		
	5.1×10^{-4}	-	5	6.23	4.3	7.21	16		
			59	6.21	4.6	7.21	16		
	-	6.1×10^{-4}	5	6.22	5.2	7.22	20		
			22	6.22	5.1	7.21	19		
	-	-	-	6.25	3.0	7.30	1.6	7.89	0.9
2-(methyl- thio)-eth- anol	1.0×10^{-4}	-	5	6.25	10 ^b	7.29	15 ^c	7.86	16
			51	6.19	9 ^b	7.25	15 ^c	7.82	16
	2.1×10^{-4}	-	5	6.26	15 ^d	f	$\frac{\text{ca}60-}{70\text{e}}$	7.9	$\frac{\text{ca}60-}{70\text{e}}$
			22	6.26	15 ^d	f	$\frac{\text{ca}60-}{70\text{e}}$	7.8	$\frac{\text{ca}60-}{70\text{e}}$
	-	1.0×10^{-4}	5	6.25	9 ^b	7.30	13 ^c	7.88	11
			67	6.24	10 ^b	7.30	13 ^c	7.87	10
	-	-	-	6.25	3.0	7.30	1.6	7.89	0.9
	-	-	-	6.25	3.0	7.30	1.6	7.89	0.9

(Contd. P.177)

Table 94 (Contd.)

Ligand	Conc. CuCl ₂ <u>M</u>	Conc. = CuCl ₄ <u>M</u>	Time after addition (mins.)	OCH ₂		SCH ₂		SCH ₃	
				τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$	τ	$\frac{\Delta\nu}{1/2c/s}$
2-(meth- ylthio)- ethanol -	-	2.1x10 ⁻⁴	6	6.24	14 ^g	7.31	15 ^c	7.84	20
	-	-	45	6.24	13 ^g	7.31	14 ^c	7.86	18
3,6-di- thia- octane				-SCH ₂ -CH ₂ S-		CH ₃ -CH ₂ S		CH ₃	
	-	-	-	7.26	0.9	7.40	1.7	8.73	1.7
	2.5x10 ⁻⁴	-	11	7.33	48 ^h	7.33	48 ^h	8.73	3.4
	4.0x10 ⁻⁴	-	11	7.34	61 ^h	7.34	61 ^h	8.73	3.4
	-	2.0x10 ⁻⁴	12	7.31	37 ^h	7.31	37 ^h	8.73	2.5
	-	4.0x10 ⁻⁴	13	7.35	61 ^h	7.35	61 ^h	8.73	3.4

- (a) OH superimposed leading to broad multiplet, - single peak line width could not be measured.
 (b) peak showing quartet splitting indicating coupling with hydroxyl, - width is combined width of two centre peaks.
 (c) peak just showing triplet splitting as shoulders.
 (d) peak showing slight centre splitting indicative of quartet structure
 (e) probably combined SCH_2 and SCH_3 peaks, - recorded peak unsymmetrical
 (f) peak showing triplet splitting at 7.27τ with a half width of 10 c/s also shown in spectrum, - probably OH
 (g) peak showing quartet splitting as outer shoulders - width includes only three highest field peaks of multiplet measured at half highest peak height
 (h) combined methylene peaks on either side of sulphur atom.

As can be seen from the results in table 94 the line broadening shown by the potential chelating ligands is much more complex than with thio-ether ligands, especially in the case of 2-(methylthio)-ethanol. In the case of thiodiglycol the small line widths shown for the SCH_2 protons indicate that copper has been reduced very rapidly from the moment of addition, probably due to traces of impurity, and so direct comparison with the other is not possible. However the results obtained definitely indicate stronger bonding to the sulphur than to the oxygen. Attempts to remove the apparent

impurity by dissolving the thiodiglycol in aqueous copper chloride and sulphate solutions, and then, after standing, to extract the thiodiglycol from the aqueous solution with chloroform failed. Repeated chloroform extraction yielded almost no thiodiglycol, indicating that the chelate formed was extremely water soluble. 2-(methylthio)-ethanol, which originally gave more marked indications of impurities (probably thiol) which reduced copper salts, was however purified by the above method and the results listed are those for the purified material. The only other ligand which required similar purification was iso-propyl sulphide.

In the case of 2-(methylthio)-ethanol the spectra obtained were rather odd inasmuch as that even in the presence of cupric chloride (and hence of methanol) the OCH_2 protons were coupled with the hydroxyl proton, appearing as a quartet. Also, as the copper concentration was increased and the peaks due to the protons adjacent to the sulphur atom collapsed, a fairly narrow triplet appeared at about the same resonance value as the original SCH_2 group, probably due to the hydroxyl proton. That this peak was in fact the hydroxyl and not the SCH_2 peak was shown by increasing the concentration of copper from that given in table 94 whence the OCH_2 peak changed from a quartet to a triplet structure, the assumed hydroxyl peak from a triplet to a singlet whilst the broad peak attributed to both the SCH_2 and SCH_3 groups almost vanished into the base line. Somewhat similar behaviour was shown in the case of thiodiglycol in which the original spectrum showed the hydroxyl proton almost co-incident with the OCH_2 peak, the latter appearing

as a broad triplet. On addition of copper however the hydroxyl proton then showed as a rather broadened singlet almost completely clear of the now only slightly broadened triplet due to the OCH_2 protons.

In the case of 3,6-dithiaoctane the protons on either side of the sulphur atom gave peaks very close to each other, and on addition of copper they broadened and overlapped. Thus in all three cases, whilst no accurate line width measurements could be obtained, it is clear that preferential collapse of protons α to the sulphur occurred, produced by co-ordination at the sulphur. While, as explained before, the results obtained with thiodiglycol must be treated with caution, in the two hydroxy-thio compounds little hydroxyl complexing occurs, bonding being predominantly through the sulphur. With 2-(methyl thio)-ethanol at least, cupric chloride is more effective in producing line broadening than the tetrachlorocuprate. Interestingly, where bidentate sulphur chelation occurs, as with 3,6-dithiaoctane, both cupric chloride and tetrachlorocuprate appear almost equally effective, presumably due to the extra strength conferred by chelation on the metal-ligand bond.

Thus, to summarise the results previously discussed in this section, whilst both cupric chloride and tetrachlorocuprate produce selective line broadening of protons α to the sulphur atom in suitable thio compounds, the relative effectiveness of the two salts depend both on the type of complex formed and on the steric environment of the sulphur atom. In relatively unhindered ligands

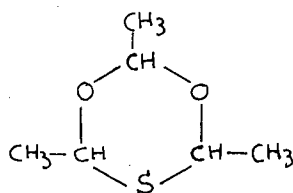
cupric chloride is only slightly more effective than tetrachlorocuprate, but when the complexes formed are less stable the cupric chloride is much more effective, the extent depending on the degree of stability of the complex. Where comparatively strong binding occurs through chelate formation the two copper species are of approximately equal effectiveness.

In order to test the usefulness of these phenomena as an aid in structural determination, various sulphur compounds were synthesised and the line broadening effect of the two copper salts studied with these and other ligands, and the results are reported in the following section.

II. Other ligands

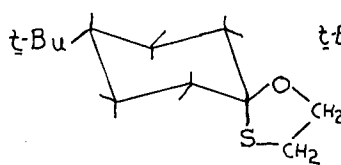
The test ligands studied fall into three groups; those containing both oxygen and sulphur in a ring system of the thiohemiketal type, substituted trithianes, and carbohydrate sulphur derivatives. As before, where no ligand concentration is given the concentration was one molar.

In the case of the thiohemiketal type compounds 2,4,6-trimethylthiadioxane (monothioparaldehyde-XXXV) and the 4-tert-butyl cyclohexanone thiohemiketals (XXXVI) the solutions containing cupric chloride faded much faster than those containing tetrachlorocuprate, and decomposition occurred with oily droplets settled out of the chloroform solution on standing for a few minutes.

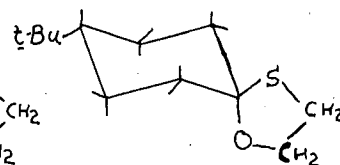


XXXV

2,4,6-trimethyl-thiadioxane



XXXVIa

4-tert-butyl-cyclohexanone thiohemiketals

XXXVIb

The original spectrum of monothioparaldehyde (XXXV) showed the ring protons as two partially overlapping quartets, the high field member of one quartet being almost co-incident with the lowest field member of the other, while the methyl group doublets were clearly distinguishable. The peaks in the spectrum were assigned by their relative intensities, and the effect of added copper (II) on their line widths are given in table 95.

Table 95. 2,4,6-trimethyl-thiadioxane

Conc. CuCl ₂ M	Conc. CuCl ₄ M	Time after addition (mins)	O-CH-S τ	$\Delta\nu 1/2^a$ c/s	O-CH-O τ	$\Delta\nu 1/2^a$ c/s	O-C(CH ₃)-S τ	$\Delta\nu 1/2^a$ c/s	O-C(CH ₃)-O τ	$\Delta\nu 1/2^a$ c/s
-	-	-	4.91	1.4	5.17	1.2	8.49	1.1	8.61	1.1
5.2 _x 10 ⁻⁴ _f	-	5 ^b 41 ^c	4.88	2.8	5.14	1.6	8.51	1.2	8.62	1.1
			4.90	1.1	5.16	1.1	8.49	0.9	8.61	0.9
1.0 _x 10 ⁻³ _f	-	5 ^d 22 ^e	4.90	3.2	5.16	1.7	8.54	1.5	8.63	1.2
			4.89	3.4	5.16	1.6	8.49	1.4	8.61	1.3
-	2.1 _x 10 ⁻³	5 25	4.89	1.7	5.16	1.6	8.49	1.1	8.61	0.9
			4.88	1.7	5.16	1.6	8.49	1.1	8.61	1.1

- (a) maximum width of individual multiplet peaks
 (b) methanol width 5.2 c/s
 (c) methanol width 1.1 c/s
 (d) methanol width 8.7 c/s
 (e) methanol width 8.4 c/s
 (f) solution yellow-green coloured.

Thus while complex formation occurred with cupric chloride judging from the colour of the solution, the degree of complexing was probably very small either due to the poor co-ordination ability of the sulphur or because the copper was rapidly reduced. In any case cupric chloride produced small, but definite selective collapse of the protons next to the sulphur whilst tetrachlorocuprate had virtually no effect. Whilst the results give little information as regards the conformation of the molecule in solution the selective collapse observed with cupric chloride tends to confirm the assignment of the peaks in the spectrum. The spectrum is interesting in that contrary to what is normally observed the proton next to the sulphur atom is at a lower field than that in which the sulphur is replaced by oxygen, the same being true for the methyl groups.

For the two epimeric 4-tert-butyl-cyclohexanone thiohemiketals (XXXVI) Eliel et al.¹⁰⁹ assigned the structure (XXXVIa) to the solid epimer and (XXXVIb) to the liquid epimer on the basis of their N.M.R. spectra, and, as can be seen from the results in table 96 this assignment is confirmed by their behaviour towards copper.

Table 96. 4-tert-butyl-cyclohexanone thiohemiketals

Epimer	Conc. CuCl ₂ M	Conc. CuCl ₄ M	Time after addition (mins)	τ	OCH ₂ $\Delta\nu$ 1/2c/s ^a	τ	SCH ₂ $\Delta\nu$ 1/2c/s ^a	τ	<u>tert</u> -butyl $\Delta\nu$ 1/2c/s
Solid	-	-	-	5.83	1.3	7.00	1.3	9.13	0.9
	1.0 x 10 ⁻²	-	1 11 ^c	5.83 5.84	12 ^b 14 ^b	7.00 6.98	>30 ^b 17 ^b	9.13 9.14	0.9 5.9 ^c
	-	4.1 x 10 ⁻³	5 20	5.82 5.82	1.7 1.7	6.96 6.96	2.6 2.6	9.14 9.14	0.9 0.9

Table 96 (Contd.)

Epimer	Conc. CuCl_2 M	Conc. CuCl_4 M	Time after addition (mins)	τ	OCH_2 $\Delta\nu$ $1/2\text{c/s}^a$	τ	SCH_2 $\Delta\nu$ $1/2\text{c/s}^a$	τ	<u>tert-butyl</u> $\Delta\nu$ $1/2\text{c/s}$
Liquid	-	-	-	5.86	1.6	6.96	1.6	9.15	0.9
	1.0 x _d	-	2	5.86	2.6	6.96	17 ^b	9.15	1.4
	10 ⁻²	-	14	5.88	1.7	6.96	3.4	9.16	1.0
	-	2.1 x	4	5.86	2.6	6.89	ca 55 ^b	9.15	0.9
	-	10 ⁻³	35	5.86	2.1	6.86	26 ^b	9.15	0.9
	-	4.2 x	5	5.86	1.6	6.94	16 ^b	9.15	0.9
	-	10 ⁻⁴	60	5.85	1.7	6.95	2.0	9.15	0.9

- (a) maximum width of individual multiplet peaks
 (b) overall band width
 (c) solution green coloured initially but after 11 mins. almost colourless and very cloudy - tert-butyl line width due to loss in resolution as cloudy oil settled out - T.M.S. width 4.1 c/s.
 (d) solution initially very dark green coloured.

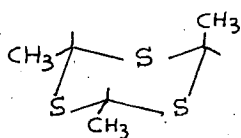
While cupric chloride produces selective collapse in both epimers, the copper is reduced extremely rapidly with decomposition of the ligand in both cases. The tetrachlorocuprate however is much more stable than the cupric chloride, the solutions retaining their golden yellow colour for more than 35 minutes. The tetrachlorocuprate is much more effective in broadening the line width in the case of the liquid epimer than in the solid epimer, the latter being virtually unaffected.

As has been mentioned before, the relative effectiveness of the tetrachlorocuprate is markedly dependent on the stereochemistry around the sulphur atom, and consideration of molecular models of the two structures (XXXVI) shows that when the sulphur is equatorial

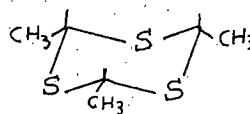
to the cyclohexane ring it is quite unhindered and so might easily complex with the chlorocopper species. When the sulphur is axial however complexing would lead to interactions between the copper and the axial protons on C3 and C6. Thus when the sulphur is equatorial complexing can easily occur, but when the sulphur is axial competition by chloride ion is relatively more important and a smaller degree of complexing would occur. The structure (XXXVIb) may then be assigned to the liquid epimer, in agreement with Eliels assignment.¹⁰⁹

The results obtained with these epimeric thiohemiketals illustrate the potential of the dependence of the extent of complexing on structure as an aid in determining the position of a sulphur atom in a molecule and the stereochemistry of the molecule in its immediate neighbourhood.

In the two isomeric 2,4,6-trimethyl-1,3,5-trithianes a similar distinction can be made, this time between axial and equatorial methyl groups. The conformation of the two isomers have been determined by electron diffraction studies to be as shown in (XXXVII).¹¹⁶



α -isomer
XXXVIIa



β -isomer
XXXVIIb

2,4,6-trimethyl-1,3,5-trithianes

The N.M.R. spectrum of the α -isomer shows two overlapping quartets due to the ring protons and two sets of methyl doublets whereas that of the symmetrical β -isomer showed only one quartet and one doublet. The methyl peaks in the spectrum of the α -isomer were assigned by relative intensity and with reference to its 40 Mc/s spectrum.¹¹¹

The results obtained with these compounds are shown in table 97 (no results could be obtained using tetrachlorocuprate for the β -isomer as almost immediately after adding $1.6 \times 10^{-3}M$ tetrachlorocuprate the colour faded and oily drops settled out from the chloroform solution).

Again tetrachlorocuprate is relatively ineffectual in causing line broadening compared to cupric chloride, at least for the α -isomer, and again cupric chloride produces broadening in both isomers. Whilst no information can be derived from the widths of the ring proton peaks for the α -isomer as the axial and equatorial quartets overlap, the relative widths of the methyl peaks are very interesting. In this isomer the methyl group axial to the ring is clearly broadened more than the methyl groups equatorial to the ring. The β -isomer, in which all the methyl groups are equatorial also gives correspondingly narrow methyl group line widths.

At first sight this selective broadening appears anomalous, but by considering a molecular model of the α -isomer the apparent anomaly may be explained in terms of relative steric hindrance at the possible complexing sites. If complexing occurs through either of the sulphur atoms adjacent to the axial methyl group there would

Table 97. trithioparaldehydes

Isomer	Conc. CuCl_2 <u>M</u>	Conc. $\text{CuCl}_4^{=}$ <u>M</u>	Time after addition (mins.)	axial CH		equat. CH		axial CH_3		equat. CH_3	
				τ	$\Delta\nu_{1/2}$ c/s ^a	τ	$\Delta\nu_{1/2}$ c/s ^a	τ	$\Delta\nu_{1/2}$ c/s ^a	τ	$\Delta\nu_{1/2}$ c/s ^a
-	-	-	-	5.50	2.6 ^b	5.63	2.6 ^b	8.11	0.9	8.48	0.9
isomer	5.2×10^{-4}	-	5	5.60	27 ^c	5.60	27 ^c	8.11	2.6	8.48	1.7
			21	5.61	26 ^c	5.61	26 ^c	8.11	2.1	8.49	1.6
	1.1×10^{-3}	-	5	5.56	29 ^d	5.56	29 ^d	8.12	4.3	8.51	2.4
			40	5.60	29 ^d	5.60	29 ^d	8.11	3.4	8.49	1.7
-	-	2.1×10^{-3}	5	5.48	4.1 ^b	5.60	4.1 ^b	8.12	1.5	8.49	1.6
			41	5.48	4.1 ^b	5.60	4.1 ^b	8.11	1.5	8.49	1.7
-	-	-	-	5.89	1.6					8.43	1.0
isomer	5.3×10^{-4}	-	5	5.83	13 ^f					8.42	1.4
			47	5.88	13 ^f					8.43	1.2
(0.54M)	1.1×10^{-3g}	-	5	5.86	22 ^h					8.42	1.7
			42	5.87	14 ^h					8.42	1.6

(a) maximum width of individual multiplet peaks unless otherwise indicated.

(b) maximum width of individual peaks of both CH multiplets.

(c) overall band width - peak showing slight centre splitting. Solution reddish brown coloured.

(d) overall band width - solution reddish brown coloured.

(e) methanol width 7 c/s.

(f) broadened quartet but showing clear splitting - width only includes two centre peaks.

(g) methanol width 10 c/s.

(h) broad quartet but showing clear central splitting - overall band width measured.

be less hindrance by the methyl groups than if complexing occurred through the remaining sulphur atom. If preferential complexing occurs at these two sulphur atoms then the axial methyl group would be effectively next to a complexing site twice as often as the other methyl groups which would be in themselves equivalent.

In order to test the usefulness of the method as an aid in analysing relatively complex N.M.R. spectra various carbohydrate sulphur derivatives were studied to see whether the protons next to the sulphur could be recognised. With these compounds only a 0.5M concentration was used due to their scarcity and the copper salts were added in small amounts to give increasing concentrations of copper, the spectra being run after each addition. The results obtained are given following under the headings of the various compounds used.

methyl β -D-1-thio-2,3,4,6-tetra-O-acetyl-mannopyranoside.

The original spectrum showed ring proton peaks centred on 4.82 τ , 5.04 τ , 5.19 τ , 5.61 τ , 6.14 τ (of relative intensity 1:(1 + 1):1:2, it being impossible to differentiate between the peaks at 5.04 τ and 5.19 τ) and a broad mass centred about 6.6 τ , with the thiomethyl and acetate peaks at 8.07 τ , 8.15 τ , 8.25 τ , 8.29 τ and 8.36 τ . On adding cupric chloride to a concentration of $2.6 \times 10^{-4}M$ a pale yellow-green solution was obtained, and the spectrum now showed ring proton peaks at 4.78 τ , 5.02 τ , 5.17 τ , 6.12 τ , with a broad 'hump' at 5.57 τ and a mass centred about 6.7 τ . The thiomethyl and acetate region now however only showed four peaks at 8.15 τ , 8.25 τ , 8.29 τ and 8.35 τ . Further addition of cupric chloride to a total

concentration of $5.3 \times 10^{-4} \text{M}$ produced no significant further change in the spectrum.

Thus the peaks at 5.61τ and 8.07τ in the original spectrum may be assigned to the anomeric proton and thiomethyl group respectively.

Addition of tetrachlorocuprate produced only little change in the spectrum compared to the effect of cupric chloride; addition up to a total concentration of $3.7 \times 10^{-3} \text{M}$ produced a spectrum which differed from the original spectrum in that it showed a broadened peak at 8.04 of about half the height of the acetate peaks. However this confirms the assignment of the thiomethyl peak. methyl β -D-1-thio-2,3,4,6-tetra-O-acetyl-glucopyranoside.

In this case a relationship between the cupric chloride and tetrachlorocuprate was found similar to the above, the former being more effective than the latter, although the tetrachlorocuprate appeared to be somewhat more effective than with the mannoside. However only the thiomethyl peak could be definitely assigned in this case, addition of copper producing only a general slight loss in resolution in the ring proton region (the ring proton region of the spectrum is much more complex and less clearly defined than in the mannoside).

The original spectrum showed peaks in the thiomethyl-acetate region at 8.17τ , 8.26τ , 8.29τ , 8.31τ and 8.34τ . Addition of cupric chloride to a concentration of $1.1 \times 10^{-4} \text{M}$ produced a broadened peak at 8.17τ , and increasing the concentration to $5.3 \times 10^{-4} \text{M}$ gave a spectrum which showed only four peaks in this

region at 8.26 τ , 8.28 τ , 8.31 τ and 8.33 τ . With tetrachlorocuprate at a concentration of $1.1 \times 10^{-3}M$ the spectrum showed a broadened peak of much reduced intensity at 8.15 and sharp peaks at 8.25 τ , 8.27 τ , 8.31 τ and 8.33 τ . Thus the peak at 8.17 τ in the original spectrum may be assigned to the thiomethyl group.

Two glucose acetate derivatives having a thiomethyl group on C6 were also studied, and here it was found that cupric chloride and tetrachlorocuprate were of comparable effectiveness. The difference in the effectiveness of the tetrachlorocuprate in the 1-thiomethyl and the 6-thiomethyl compounds thus reflects the greater steric hindrance and smaller electron availability in the thioglycosides. methyl β -D-2,3,4-tri-O-acetyl-6-deoxy-6-thiomethyl-glucopyranoside.

The original spectrum showed the ring proton region of very low intensity and two fairly intense peaks at 7.65 τ and 7.73 τ of a combined relative intensity of two, with the methoxyl peak at 6.86 τ and the thiomethyl and acetate peaks at 8.14 τ , 8.25 τ , 8.28 τ and 8.32 τ . Cupric chloride at $1.1 \times 10^{-4}M$ concentration and tetrachlorocuprate at a concentration of $2.1 \times 10^{-4}M$ produced the same results, the spectrum now only showing peaks at 6.86 τ , 8.27 τ , 8.30 τ and 8.34 τ . Thus the peaks at 7.65 τ and 7.73 τ may be assigned to the protons on C6, and that at 8.14 τ to the thiomethyl group. 1,2,3,4-tetra-O-acetyl- β -D-6-deoxy-6-thiomethyl-glucopyranoside.

In the region of interest the original spectrum showed peaks at 7.64 τ and 7.73 τ , 8.19 τ , 8.22 τ , 8.29 τ , 8.31 τ and 8.33 τ . Again $1.1 \times 10^{-4}M$ cupric chloride and $2.1 \times 10^{-4}M$ tetrachlorocuprate produced identical results in eliminating the peaks due to the

protons next to the sulphur, the spectra now only showing peaks at 8.23 τ , 8.30 τ , 8.31 τ and 8.33 τ . Thus the protons on C6 may be assigned to the peaks at 7.64 τ and 7.73 τ and the thiomethyl group to that at 8.19 τ .

Thus the method of selective collapse may be used to identify peaks in spectra arising from protons on carbon atoms adjacent to a sulphur atom.

B. Aqueous solution.

As previously mentioned in section 4(III)(b), in aqueous solution very little selective sulphide complexing occurred in thiodiglycol with copper (II) in the absence of added excess chloride. In order to test the feasibility of identifying the location of protons adjacent to the sulphur atom in sulphur compounds various compounds were studied in aqueous solution with various concentrations of copper and chloride. Thiodiglycol and 2-(methyl thio)-ethanol were studied with both cupric perchlorate and cupric chloride, and various carbohydrate sulphur derivatives studied with cupric chloride only and the results are discussed below. The former two compounds were studied at 1M and the carbohydrate derivatives at approximately 0.5M concentrations. The reference standard used was tert-butanol taken as having a resonance value of 8.77 τ .

Table 98. Thiodiglycol

Anion	Conc. Cu(II) <u>M</u>	Conc. KCl <u>M</u>	Time after addition (mins.)	HOD τ	$\Delta\nu_{1/2}$ c/s	OCH ₂ τ	$\Delta\nu_{1/2}$ c/s	SCH ₂ τ	$\Delta\nu_{1/2}$ c/s	Colour of soln.
-	-	-	-	5.30	1.1	6.25	1.7 ^a	7.26	1.6 ^a	colourless
perchl- orate	1.0×10^{-3}	-	3 47	5.30 5.31	1.8 1.7	6.25 6.24	16 ^b 14.5 ^c	7.22 7.21	19 ^b 17 ^b	colourless
chloride	1.0×10^{-3}	-	5 54	5.32 5.31	1.6 1.1	6.25 6.25	15 ^c 5.1 ^d	7.22 7.24	16.4 ^b 15.5 ^b	colourless
chloride	1.0×10^{-3}	1.0	5 42	5.39 5.40	1.6 0.9	6.25 6.25	4.9 ^d 3.1 ^a	7.21 7.21	24 22	very pale yellow green
chloride	1.0×10^{-3}	2.0	5 44	5.47 5.48	1.6 0.9	6.25 6.24	5.2 ^d 3.4 ^a	7.20 7.19	33 30	yellow green

- (a) maximum width of individual multiplet peaks.
 (b) peak just showing triplet splitting as shoulders.
 (c) peak showing clear triplet splitting.
 (d) width of centre peak of triplet.

Table 99. 2-(methylthio)-ethanol

Anion	Conc. Cu(II) <u>M</u>	Conc. KCl. <u>M</u>	Time after addit- ion (mins)	HOD $\Delta v_{1/2}$ c/s	OCH ₂ $\Delta v_{1/2}$ c/s	SCH ₂ $\Delta v_{1/2}$ c/s	SCH ₃ $\Delta v_{1/2}$ c/s	Colour of soln.				
-	-	-	-	5.32	0.9	6.24	1.6 ^a	7.31	1.9 ^a	7.89	0.9	colourless
per- chlorate	1.0x10 ⁻³	-	4 37	5.32 5.32	1.5 1.3	6.23 6.24	15.4 ^b 14 ^c	7.29 7.29	17 ^b 15 ^b	7.85 7.86	9.4 8.6	colourless
chloride	1.0x10 ⁻³	-	5 61	5.30 5.28	1.4 1.6	6.24 6.25	16 ^b 15.5 ^b	7.30 7.30	16.4 ^b 15.5 ^b	7.87 7.87	10.4 9.5	colourless
chloride	1.0x10 ⁻³	1.0	5 40	5.40 5.42	1.6 0.9	6.29 6.25	10.7 ^c 3.4 ^d	7.3 7.3	61 ^e 60 ^e	7.83 7.83	61 ^e 60 ^e	pale yellow- green
chloride	2.6 x10 ⁻⁴	-	5 33	5.31 5.31	1.7 1.7	6.24 6.25	4.8 ^d 4.3 ^d	7.32 7.31	3.4 ^a 2.8 ^a	7.87 7.88	3.6 3.6	colourless
chloride	2.6x10 ⁻⁴	2.0	5 45	5.39 5.53	1.6 1.3	6.24 6.25	3.9 ^d 2.8 ^a	7.28 7.26	25 ^f 22 ^f	7.85 7.85	24 ^f 18 ^f	yellow green

- (a) maximum width of individual peaks in multiplet.
 (b) peak just showing triplet splitting as shoulders.
 (c) peak showing clear triplet splitting
 (d) width of centre peak of multiplet.
 (e) combined width of SCH₂ and SCH₃ peaks measured at half SCH₃ peak height.
 (f) peaks partially overlapping.

As can be seen from the results in tables 98 and 99 the line widths obtained with thiodiglycol and 2-(methylthio)-ethanol in aqueous solution containing excess chloride ion are qualitatively similar to those obtained in chloroform solution. The greater line widths obtained for 2-(methylthio)-ethanol than for thiodiglycol would tend to indicate that the latter shows a greater tendency towards chelate formation, such chelation reducing the tendency towards monodentate sulphur complexing, or else that the greater steric hindrance in thiodiglycol depresses the extent of sulphur complexing. Comparison of the OCH_2 line widths in solutions containing 1M chloride and 10^{-3}M copper, in which the 2-(methylthio)-ethanol line width is greater would tend to show that the latter explanation is more probable, and that the thiodiglycol complexes to a lesser degree overall. The results also show that 'fading' occurs in aqueous solution as well as in chloroform solution, with removal of copper (II).

Again, the selective collapse phenomenon was studied in various trial compounds in order to assess its suitability as an aid in both structural determination and in analysis of the ligand N.M.R. spectra. The results are reported in tables 100 to 103.

Table 100. methyl- β -D-1-thio-glucopyranoside

Time mins.	Time of CuCl_2 addition (mins)	Total CuCl_2 conc. M	Conc. KCl . M	τ	HOD $\Delta\nu 1/2\text{c/s}$	τ	SCH_3 $\Delta\nu 1/2\text{c/s}$	peak height ^a
0		-	-	5.30	1.6	7.79	1.3	65
2	0	2.6×10^{-4}	-	5.32	2.3	7.79	1.7	40
6		"	-	5.32	2.5	7.79	1.7	40

(Contd. P.194)

Table 100 (Contd.)

Time mins.	Time of CuCl ₂ addition (mins.)	Total CuCl ₂ conc. \underline{M}	Conc. KCl \underline{M}		HOD ΔV 1/2c/s		SCH ₃ ΔV 1/2c/s	peak height ^a
10	8	5.2 x 10 ⁻⁴	-	5.31	3.3	7.79	1.9	35
13		"	-	5.30	2.8	7.79	1.9	35
19	17	1.0 x 10 ⁻³	-	5.31	1.9	7.79	2.2	31
23		"	-	5.30	2.8	7.78	2.2	31
0		-	2.0	5.47	2.6	7.78	1.4	62
4	0	2.6 x 10 ⁻⁴	2.0	5.49	2.3	7.78	1.7	40
8		"	"	5.48	2.0	7.78	1.7	40
14	11	5.2 x 10 ⁻⁴	"	5.49	1.9	7.78	1.7	37
18		"	"	5.49	1.9	7.78	1.8	37
25	21	1.0 x 10 ⁻³	"	5.48	2.2	7.77	2.2	30
31		"	"	5.48	2.4	7.78	2.3	30

(a) height at constant recorder gain and constant r.f. power.

Here no significant preferential broadening of the thiomethyl peak was obtained as compared with the solvent peak, but a definite and clearly noticeable diminution in the peak intensity was obtained. While this is indicative of some degree of complex formation occurring any such complexing must be of small extent. Very similar behaviour was shown by the corresponding galactoside as shown in table 101.

Table 101. methyl β -D-1-thio-galactopyranoside

Time mins.	Time of CuCl ₂ addition (mins.)	Total CuCl ₂ conc. \underline{M}	Conc. KCl. \underline{M}		HOD ΔV 1/2c/s		SCH ₃ ΔV 1/2c/s	peak height ^a
0	-	-	-	5.30	0.9	7.78	1.3	72
2	5	2.6 x 10 ⁻⁴	-	5.30	2.1	7.77	2.0	34
5		"	-	5.31	1.9	7.78	1.9	34

(Contd. P.195)

Table 101 (Contd.)

Time mins.	Time of CuCl_2 addition (mins.)	Total CuCl_2 conc. $\underline{\text{M}}$	Conc. KCl . $\underline{\text{M}}$	τ	HOD ΔV 1/2c/s	τ	SCH_3 ΔV 1/2c/s	peak height ^a
9	7	5.2×10^{-4}	-	5.30	2.2	7.77	2.4	31
12		"	-	5.31	2.4	7.77	2.6	30
17	16	1.0×10^{-3}	-	5.29	2.4	7.77	2.8	26
21			-	5.31	2.5	7.77	2.8	26
0	-	-	-	5.49	1.6	7.77	1.1	76
2	0	2.6×10^{-4}	2.0	5.49	2.3	7.77	2.0	35
7		"	"	5.50	2.3	7.77	2.0	35
11	9	5.2×10^{-4}	"	5.48	2.2	7.76	1.8	36
14		"	"	5.49	2.2	7.77	1.8	35
19	16	1.0×10^{-3}	"	5.49	2.3	7.76	2.1	35
22			"	5.49	2.3	7.77	2.2	35

(a) peak height at constant recorder gain and constant r.f. power.

While no significant broadening occurred in the methyl glycosides, with mannose-dimethyl-dithioacetal and mannose-ethylene-dithioacetal relatively extensive broadening was obtained, again accompanied by a diminution in peak height (tables 102 and 103) respectively).

Table 102. mannose-dimethyl-dithioacetal

Time mins.	Time of CuCl_2 addition (mins.)	Total CuCl_2 conc. $\underline{\text{M}}$	Conc. KCl . $\underline{\text{M}}$	τ	HOD ΔV 1/2c/s	τ	SCH_3 ΔV 1/2c/s	peak height ^a
0	-	-	-	5.30	1.7	7.74, 7.76	$<2.6^b$	84
2	0	2.7×10^{-4}	-	5.31	1.7	7.74	2.7	60
5		"	-	5.31	1.6	7.74	2.6	60
9	8	5.3×10^{-4}	-	5.24	1.7	7.74	2.8	52
12		"	-	5.26	1.7	7.74	2.9	53

(Contd. P. 196)

Table 102 (Contd.)

Time mins.	Time of CuCl ₂ addition (mins.)	Total CuCl ₂ conc. \underline{M}	Conc. KCl. \underline{M}	HOD τ	$\Delta\nu$ 1/2c/s	SCH ₃ τ	$\Delta\nu$ 1/2c/s	peak height ^a
19	16	1.1×10^{-3}	-	5.29	1.9	7.74	3.4	47
21		"	-	5.30	1.7	7.74	3.4	47
0	-	-	2.0	5.47	1.7	7.73, 7.74	<2.4 ^b	54
2	0	2.7×10^{-4}	2.0	5.48	1.7	7.74	3.4	30
5		"	"	5.48	1.7	7.74	3.4	31
11	9	5.3×10^{-4}	"	5.46	1.7	7.72	4.3	28
15		"	"	5.48	1.6	7.74	4.3	27
21	19	1.1×10^{-3}	"	5.48	1.7	7.74	5.4	21
24		"	"	5.47	1.7	7.74	5.4	21

(a) peak height at constant recorder gain and constant r.f. power.

(b) total band width at half highest peak height measured.

In the two glycosides and the mannose-dimethyl-dithioacetal the H1 proton peak could not be observed clearly, being at least partially obscured by the solvent resonance, but in the mannose-ethylene-dithioacetal where the peak is clearly visible relatively extensive selective broadening occurs. The greater degree of broadening shown in the mannose thioacetals is probably due to there being somewhat less steric hindrance around the sulphur atoms coupled with the fact that in the two glycosides the electron withdrawing nature of the ring oxygen would tend to reduce the electron availability at the sulphur atom so leading to a smaller degree of complexing.

Thus while the degree of line broadening observed in aqueous solution, even in the presence of a very large excess of chloride ion, is much smaller than that observed in chloroform solution, the method

Table 103. mannose-ethylene-dithioacetal

Time mins.	Time of CuCl ₂ addition (mins.)	Total CuCl ₂ conc. M	Conc. KCl. M	HOD τ	ΔV 1/2c/s	SCH ₂ CH ₂ S ΔV 1/2c/s	τ	peak height ^a	H1 τ	ΔV 1/2c/s ^b
0	-	-	-	5.31	1.1	6.72	2.2	89	5.01	3.4
2	0	2.7 x 10 ⁻⁴	-	5.26	1.7	6.72	2.7	69	5.02	4.1
5		"	-	5.32	1.7	6.72	2.8	68	5.01	3.8
10	8	5.3 x 10 ⁻⁴	-	5.29	1.7	6.72	3.1	62	5.06	4.0
13		"	-	5.31	1.7	6.72	3.2	62	5.04	4.0
18	16	1.1 x 10 ⁻⁴	-	5.31	1.7	6.72	3.4	55	4.99	4.3
21			-	5.31	1.7	6.72	3.4	56	5.00	4.3
0	-	-	2.0	5.48	1.4	6.71	2.3	98	5.01	3.7
2	0	2.7 x 10 ⁻⁴	"	5.48	1.7	6.68	3.3	45	5.01	5.6
6		"	"	5.50	1.7	6.74	3.4	46	4.99	6.0
11	9	5.3 x 10 ⁻⁴	"	5.48	1.7	6.70	4.3	37	5.01	7.8
14		"	"	5.48	1.7	6.71	4.3	34	5.01	7.8
20	17	1.1 x 10 ⁻³	"	5.47	1.7	6.70	5.3	25	ca5.0	c
23		"	"	5.48	1.8	6.71	5.3	24	ca5.0	c

(a) peak height at constant recorder gain and constant r.f. power.

(b) total band width.

(c) peak too broad to measure - almost broadened into base line.

has potential use in assisting in the analysis of the N.M.R. spectra of sulphur containing compounds. By this method the peaks in a spectrum corresponding to protons situated on carbon atoms adjacent to the sulphur atom may be assigned in favourable cases.

The potential of the method however is much greater for chloroform soluble sulphur compounds as the sensitivity is greatly increased in this solvent. Whilst the assignment of protons situated adjacent to a sulphur atom may be accomplished easily, the greater importance of the method lies in the capability of distinguishing between sulphur atoms in different environments both within the same molecule and in different molecules. Thus distinction could be made between chain branching α - and β - to a sulphur atom, between a thioether and a disulphide, and indeed the presence of an accessible sulphur atom in a molecule could be established. The method may also be used to facilitate analysis of a complex N.M.R. spectrum in which the resonances of protons adjacent to a sulphur atom overlap and partially obscure those of other protons. Thus by adding sufficient copper (II) to completely broaden and remove the resonances of the proton next to the sulphur the spectrum of the remaining protons could then be observed in isolation.

In view of the rather wide potential use of the method of selective collapse, preliminary studies were undertaken in order to determine whether this could be extended to other systems. The preliminary conclusions drawn from these studies are discussed briefly in the following section, part 5.

PART 5: SELECTIVE BROADENING IN ALCOHOLS, ACIDS AND AZINES -
PRELIMINARY STUDIES

In view of the great selective collapse shown in sulphide ligands in the presence of copper (II), the effects of copper (II) on alcohols and acids were studied in a preliminary manner. The effect of gadolinium (III) was also investigated.

In these systems, in order to study chloroform soluble ligands the metal ions had to be added as a methanol solution such that sufficient methanol was present to keep the metal ion in solution. The metal salts were consequently added from stock solutions of $M/20$ concentration and this meant that competition between ligand and carrier occurred. While the degree of broadening of the methanol methyl peak was indicative of the extent of complexing, the fact that exchange averaging occurred between the hydroxyl group of the methanol and the ligand hydroxyl or carboxyl proton rendered meaningful interpretation of the degree of broadening of this averaged peak impossible. In order to try to avoid this averaging mechanism by dispensing with the methanol carrier cupric acetylacetonate was tested as a possible complexing agent but it was found to be virtually ineffective. Consequently cupric chloride and acetate and gadolinium trichloride were used.

The simple ligands studied were purposefully chosen so as to give spectra consisting mainly of singlet resonances in order to render comparison of line widths easier. Ligands such as acetic, methoxyacetic and *p*-methoxyphenyl acetic acids, diacetone alcohol and *p*-methoxybenzyl alcohol being mainly studied although some

other simple alcohols and acids were also investigated more briefly.

Of the three paramagnetic compounds studied gadolinium was found to be more effective in producing line broadening than any of the two copper salts, broadening not only the averaged hydroxyl proton resonance and methanol peak but also the protons on the carbon atom α - to the hydroxyl or carboxyl group of the ligand. The broadening of the α -protons was greater for acids than for the corresponding alcohols and was clearly selective, the other peaks in the spectra being virtually unaffected, except at a relatively high gadolinium concentration where general loss in resolution and some precipitation usually occurred (ca. $5 \times 10^{-4} \text{M}$ or greater).

With the two copper salts higher metal concentrations could be added without precipitation occurring, in these studies concentrations up to 10^{-3}M being used. At such concentrations interesting differences in behaviour between cupric chloride and cupric acetate were observed. With simple acids as ligands the acetate produced fairly marked selective broadening of the protons adjacent to the carboxyl group but the chloride had relatively little effect (e.g. with methoxy acetic acid the CH_2 line width increased from 1.2 to 3.3 c/s at 10^{-3}M concentration with the acetate but only from 1.1 to 1.6 c/s with the chloride). With alcohols however the order of effectiveness was found to be inverted, the chloride producing greater broadening of the protons next to the hydroxyl group. For example, with diacetone alcohol ($\text{CH}_3\text{-CO-CH}_2\text{-C(CH}_3)_2\text{OH}$) the line width of the CH_2 protons increased from 1.7 c/s to 2.1 c/s at 10^{-3}M

concentration of the chloride but was unaffected by the same concentration of the acetate. With this ligand the widths of the averaged hydroxyl resonance and of the methyl group of the methanol carrier were also greater in the presence of the chloride; in the presence of the acetate whilst the hydroxyl peak was extensively broadened the methanol methyl group resonance was virtually unaffected even at 10^{-3}M copper concentration.

While the extent of selective collapse obtained with alcohols and acids as ligands was found to be very much less than that with sulphide ligands the extent of collapse exhibited by ethylnicotinate was found to be even more spectacular. Thus with a 0.4M solution of ethyl nicotinate (instead of the 1M concentration used for the acids and alcohols) addition of about $5 \times 10^{-5}\text{M}$ cupric chloride almost completely removed the resonances due to H_2 and H_6 , seriously reduced the resolution of the H_5 multiplet yet left that due to H_4 virtually unaffected.

Thus while the results of these studies are only preliminary and require confirmation from a wider study, they nevertheless indicate that the method of selective collapse could be of use in the study of acids and alcohols, especially using gadolinium (III). The indications are that the presence of hydroxyl and carboxyl functional groups within a molecule might be detected by such methods, and the groups immediately adjacent to such groups recognised in their N.M.R. spectra. The apparent difference in behaviour of cupric chloride and cupric acetate towards such ligands might also merit further study although it was found that methanolic solutions

of cupric acetate deposited greyish-white crystals on prolonged standing. However the use of freshly made up solutions would probably circumvent such loss of copper by what is presumably a solvolysis reaction. However it is in the study of azine type compounds that the utility of the method appears more apparent. In such compounds, by successive increase in the concentration of cupric chloride it might be possible to identify the protons α -, then β - etc. to the nitrogen atom and so perhaps lead to a complete assignment of the peaks in a spectrum. In favourable compounds positions of substitution might also be ascertained.

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