Structure and Stability of Carboxylate Complexes. Part XII.[1] The Location of Co-ordination Sites in Copper(II) Carboxylates in Solution by Proton Magnetic Resonance

By **Keith B. Dillon** and **Francis J. C. Rossotti,*** Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR

Differential proton relaxation has been used to locate binding sites for copper(II) in 35 carboxylate ligands with distinguishable proton magnetic resonance signals. Relaxation rates in aqueous solution have been shown to decrease with increasing distance from the co-ordinated cation in a series of unequivocally unidentate monocarboxylate ligands. 2- and 3-Hydroxy- and 2-alkoxy-carboxylates are predominantly bidentate towards copper(II), whereas 4-hydroxy- and 3-alkoxy-carboxylates are predominantly unidentate. The dicarboxylates malonate, succinate, 2-methylmalate, and diglycollate all appear to be bidentate.

The relative dipolar and scalar contributions to the proton spin–spin relaxation have been assessed in the acetate and butyrate systems.

THE structures of metal-ion complexes may be determined unequivocally in the solid state by X-ray crystallography. However, a complex will not necessarily retain the same structure in solution and may even have different structures in different solvents. It is not easy to determine structures in solution and these have often been inferred from thermodynamic data.[2,3] A correlation of the stability constants for corresponding copper(II) and hydrogen-ion complexes of some aliphatic monocarboxylates, determined potentiometrically in a 3M-sodium perchlorate medium at 25·00 ± 0·05 °C, has shown [4] that 2-hydroxy-, 2-alkoxy-, 2-aryloxy-, and 3-hydroxy-carboxylates form more stable copper(II) complexes than unsubstituted or halogeno-carboxylates with similar pK_a values. All the ligands, which give enhanced stability, have a potential oxygen donor atom other than that in the carboxy-group and a chelated structure is possible. Similar observations have been made by other workers for carboxylate complexes of different metal ions.[3] The differences in stability for all but the 2-hydroxy-systems are small, however, and mainly reflect differences in the ligational enthalpy. There is little entropic discrimination between the formation of copper(II) monocarboxylates, which are acyclic and those which may be cyclic,[5] although the ' chelate effect ' is mainly entropic.[3]

In the solid state, we have shown that glycollate,[6] lactate,[6] 2-hydroxyisobutyrate,[6] methoxyacetate,[6] ethoxyacetate,[7] and phenoxyacetate [6] form chelated copper(II) complexes. These compounds have magnetic moments of *ca.* 1·9 B.M. By contrast, 3-hydroxy- and -alkoxy-carboxylates have lower magnetic moments,[8] the temperature dependence of which is indicative of dimeric copper acetate-type structures. Hence these species, which are monomeric in aqueous solution,[4] might be expected to have different structures from the 2-substituted carboxylates in solution and a direct determination of the structures in that medium was desirable.

The intense fluctuating magnetic fields, set up by motions of unpaired electrons, on addition of paramagnetic metal ions to a ligand solution shorten both the longitudinal (spin–lattice) relaxation time and the transverse (spin–spin) relaxation time of ligand nuclei with a magnetic moment. The result is a broadening of the resonances. There are two possible mechanisms for the interaction, a dipolar interaction inversely proportional to the sixth power of the distance between the magnetic dipoles, and a scalar coupling of the proton and electron spins. Scalar coupling occurs if there is a partial delocalisation of unpaired electron density into ligand orbitals. Its distance dependence is not known, but it has been considered to be of secondary importance to the dipolar mechanism in causing relaxation of nuclei in the outer co-ordination sphere.[9]

Li and his co-workers postulated [10] that paramagnetic metal ions should selectively broaden the resonances of ligand nuclei adjacent to co-ordination sites, and used this effect to study transition-metal complexes of various organic ligands.[11-14] Similar investigations were carried out by Cohn and Hughes [15] and subsequent workers. All these studies were essentially qualitative. A systematic study of copper(II) carboxylate complexes has now been undertaken on a more quantitative basis, in order to elucidate structures in solution. A preliminary account of this work has been given elsewhere.[16]

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THEORY

For a Lorentzian absorption signal of a particular proton *in* a ligand, the experimental transverse relaxation time T is related to the full width of the signal $\Delta\nu$ (in Hertz) at half-height by the equation:

$$1/T = \pi\Delta\nu \qquad (1)$$

In a solution containing paramagnetic metal ions B in stepwise equilibrium

$$\mathrm{B} + n\mathrm{A} \rightleftharpoons \mathrm{BA}_n \quad (0 \leqslant n \leqslant N)$$

with ligands A, exchange reactions

$$\mathrm{BA}_n + \mathrm{A}^* \underset{\tau_n}{\rightleftharpoons} \mathrm{BA}_{n-1}\mathrm{A}^* + \mathrm{A}$$

occur, where τ_n is the mean life time of the ligand in the complex BA_n. The linewidths of the resonances of the ligand protons will be determined [17,18] by the relative magnitudes of the relaxation rates $1/T_n$ and $1/T_\mathrm{A}$ for the protons in co-ordinated ligands and free ligand, respectively, and the exchange rate constants $1/\tau_n$. The Bloch equations have been modified by McConnell [19] to include the effects of chemical exchange. On the assumption that τ_n and T_n are very much greater than the electron-spin relaxation time (rapid spin exchange), we may write

$$\frac{1}{T} = \frac{A - \bar{n}B}{AT_\mathrm{A}} + \frac{1}{A}\sum_{1}^{N}\frac{n[\mathrm{BA}_n]}{T_n + \tau_n} \qquad (2)$$

cf. reference.[18] We now set

$$n[\mathrm{BA}_n] = \bar{n}B$$

where $\bar{n}$ is the average number of bound ligands per metal ion,[20] and write T_B and τ_B as the appropriate weighted averages of T_n and τ_n respectively (or, more crudely, regard the last two parameters as independent of the value of n). Hence:

$$\frac{1}{T} = \frac{1}{T_\mathrm{A}} + \frac{B\bar{n}}{A}\left(\frac{1}{T_\mathrm{B} + \tau_\mathrm{B}} - \frac{1}{T_\mathrm{A}}\right) \qquad (3)$$

If $\tau_\mathrm{B} \gg T_\mathrm{B}$ in equation (3), exchange will be rate-determining and the equation resembles that of McConnell and Berger.[21] If, however, $T_\mathrm{B} \gg \tau_\mathrm{B}$, relaxation is dominant, leading to the type of equation first developed by Bloembergen, Purcell, and Pound [22] and extended by later workers.[23]

Ligand-exchange rates for copper(II) complexes with oxygen donor ligands are rapid [24] and the mean lifetimes τ_B ($\sim 10^{-8}$ s) are much shorter than the experimental values of $1/(T_\mathrm{B} + \tau_\mathrm{B})$ (10^{-2} to 10^{-5} s) found in the present work. Hence, relaxation is dominant for protons in ligands with oxygen donor atoms, as has been noted previously by Pearson and Lanier.[18] Moreover, $1/T_\mathrm{B} \gg 1/T_\mathrm{A}$ so that equation (3) may be simplified and combined with equation (1) to yield, for each proton signal,

$$\Delta\nu = \Delta\nu_i + B\bar{n}/AT_i \qquad (4)$$

where $\Delta\nu_i$ is now the linewidth for protons on the i-th carbon atom ($^-\mathrm{CO_2}^- = 1$) in the free ligand and T_i the transverse relaxation time for those protons in bound ligand. If $A \gg \bar{n}B$ the free ligand concentration and hence $\bar{n}$ will be constant [20] so that linear functions $\Delta\nu(B)_{A,\bar{n}}$ may readily be obtained experimentally and values of $\bar{n}/T_i$ obtained from their slopes.

The above derivation of equation (4) has neglected outer-sphere relaxation. More rigorously, the experimentally determined parameter will be $\bar{n}/(T_i + T_0)$ where T_0 is a relaxation time averaged over the protons on the i-th carbon atom in all ligands within the sphere of influence of the paramagnetic ion, but outside the inner co-ordination sphere. Pearson and his coworkers [17] have estimated $T_0/T_i \sim 0{\cdot}07$ for both the $\mathrm{CH_3}$ and OH proton signals of methanol by replacing $\mathrm{Cu^{II}}$ by its substitution inert complex $\mathrm{Cu(bipy)_3}^{2+}$. Consequently, the neglect of T_0 cannot be serious for protons in carboxylates, as dipolar interaction decreases inversely as the sixth power of distance.

EXPERIMENTAL

Solutions.—Carboxylate buffer solutions were prepared from either alkali-metal salts or known amounts of the carboxylic acid and AnalaR potassium carbonate. Water or $\mathrm{D_2O}$ were used as solvents, depending on the chemical shifts of the ligand resonances. For the monocarboxylates, pH was held $\leqslant 5$ in order to avoid hydrolysis of copper(II). For the dicarboxylates, the pH was chosen to give largely dianionic free ligand in order to avoid the formation of protonated metal complexes. The ligand concentration was in the range $0{\cdot}4 \leqslant A \leqslant 0{\cdot}8\mathrm{M}$, except for carboxylates of limited solubility, and was kept constant for measurements on any one system. The required copper concentration, in the range $0 \leqslant B \leqslant 2$ mM, was obtained by adding either an aqueous solution of copper(II) perchlorate or a $\mathrm{D_2O}$ solution of copper chloride from an Agla micrometer syringe. Under these conditions, free ligand was in considerable excess of bound ligand, and remained essentially constant for any one system as B was increased.

Acids of the best available commercial grade were used, and the purity was checked, if in doubt, by alkalimetric titration. Sodium 3-methoxypropionate and 3-ethoxypropionate were prepared by alkaline hydrolysis of the corresponding nitriles, and sodium 4-hydroxybutyrate and 4-hydroxyvalerate by hydrolysis of the 4-lactones. Other alkali-metal salts were prepared from the acids according to the method of Childers and Struthers,[25] or by minor modifications of their process.

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Buffer solutions of halogenocarboxylates were prepared immediately prior to the recording of the spectra, in order to avoid hydrolysis to the corresponding hydroxy-analogue. Hydrolysis would have resulted in the appearance of new signals in the spectrum, and was not detected except in the 2-bromoisobutyrate and 4-chlorobutyrate systems, where some hydrolysis occurs even during a period of 15 min. De Barr reported [26] that 4-chlorobutyric acid was hydrolysed more rapidly than trichloroacetic acid, and hydrolysis of 2-bromoisobutyrate is probably favoured by both steric and inductive effects.

Spectroscopy.—The high resolution n.m.r. spectra were recorded on a Perkin-Elmer R10 60 MHz spectrometer by Mrs. E. E. Richards or her assistants, at 34·2 °C. Chemical shifts were noted using TSS * as internal reference. Rapid exchange with solvent precluded observation of hydroxy or carboxy proton signals and measurements are reported for the CH_n group resonances only. The peak widths were measured and plotted as a function of B for each system. Values of $\bar{n}/T_i$ could then be calculated from the slopes of the linear plots according to equation (4). No variation of linewidth with R.F. field or sweep rate was observed in test solutions, showing that saturation broadening was absent.

For spin–spin multiplets, measurements were usually made on the most intense signal, in order to avoid the resolution necessary to allow for partial collapse of the multiplet structure with consequent overlapping of the components. However, resolution was sometimes necessary at the higher copper(II) concentrations. Frequent checks were carried out by measuring the linewidths of two or more components from the same multiplet as a function of copper concentration. Plots of identical slope were usually obtained within experimental error, but occasional divergences were found with very unsymmetrical multiplets. An average value for the width at half-height was then taken.

The relative contributions of the dipolar and scalar terms of the relaxation in the acetate system were investigated (by Dr. D. J. Bell) by determining T_l and T_t by spin-echo methods over the temperature range $273 < K < 344$ at 20 MHz and $279 < K < 315$ at 35 MHz.

RESULTS AND DISCUSSION

Relaxation control has been confirmed for the copper(II) acetate system by measurement of the temperature dependence of both the longitudinal and transverse relaxation times (see below p. 1012). An increase in temperature should reduce τ_n, since τ_n^{-1} is a rate constant for a chemical reaction. The transverse relaxation time would increase with temperature, if correlation were limited by the rotational tumbling time of the complexes, although a small decrease would be expected if electron-spin exchange were the limiting factor.[17] The longitudinal and transverse relaxation times for a D_2O solution of sodium acetate with added copper(II) chloride were determined at various temperatures between 5 and 70 °C by spin-echo methods; both increased with increasing temperature. Checks of the temperature dependence of $\Delta\nu$ for other copper(II) systems [27] indicate that relaxation control is common and that the approximation involved in deriving equation (4) from equation (3) is justified.

For any one carboxylate, the average ligand number $\bar{n}$ is identical for all resonances, and changes in $\bar{n}/T_i$ according to the position of the group will be due solely to changes in $1/T_i$. To compare results for different systems, it is necessary to consider the differences in $\bar{n}$ also. If mononuclear complexes only are formed, and the stability constants are known, together with the free ligand concentration a, $\bar{n}$ may be calculated from the equation: [20]

$$\bar{n} = \frac{\sum_{1}^{N} n\beta_n a^n}{\sum_{0}^{N} \beta_n a^n}$$

Values were thus calculated using the stability constants determined [4] in a 3M-sodium perchlorate medium at 25 °C. Values were also calculated for the same values of a, using the stability constants determined by Fronaeus [28] for the copper(II) acetate, glycollate, and chloroacetate systems and by Sandell [29] for the copper(II) methoxyacetate and ethoxyacetate systems in a 1M-sodium perchlorate medium at 20 °C. For all systems except phenylacetate, where a very low value of A (0·1M) was used because of limited solubility, the $\bar{n}$ values from both sets of data were within a factor of two, ranging from 1·46 for cyanoacetate to 2·83 for glycollate. The observed variations in $\bar{n}/T_i$ are much greater and cannot be due to changes in $\bar{n}$ alone. Neither of the sets of $\bar{n}$ values can be applied rigorously to the n.m.r. data, since these experiments were not carried out in a constant ionic medium or at the same temperature as was used in the determination of the stability constants. Nevertheless, a similar range of values of $\bar{n}$ will be expected in the n.m.r. solutions.

Unsubstituted Carboxylates.—In an unsubstituted carboxylate ligand with more than one proton signal, the broadening decreases with distance from the carboxy-group. This decrease is illustrated for propionate in Figure 1 and is as expected from the distance dependence of the interaction, since the carboxy group is the unique co-ordination site in these ligands. The values of n/T_i calculated for acetate, propionate, and butyrate are given in Table 1.

TABLE 1

Relative proton relaxation rates (s^{-1}) for unsubstituted monocarboxylates

	A/mM	$10^{-3}\bar{n}/T_2$	$10^{-3}\bar{n}/T_3$	$10^{-3}\bar{n}/T_4$
Acetate	505	4·5		
Propionate	680	4·3	1·9	
Butyrate	520	4·4	1·5	0·5

Halogenocarboxylates.—The same sequence is observed as in the unsubstituted carboxylates, irrespective

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* Sodium 3-(trimethylsilyl)propanesulphonate.

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of the position of the halogen in the chain. We therefore conclude that these ligands are all predominantly unidentate with respect to copper(II) ions. The calculated results are given in Table 2. The widths of the 2- and 3-methylene resonances of 4-chlorobutyrate could not be measured owing to overlapping * of the spin–spin multiplets with each other and with the resonances of the hydrolysis product.

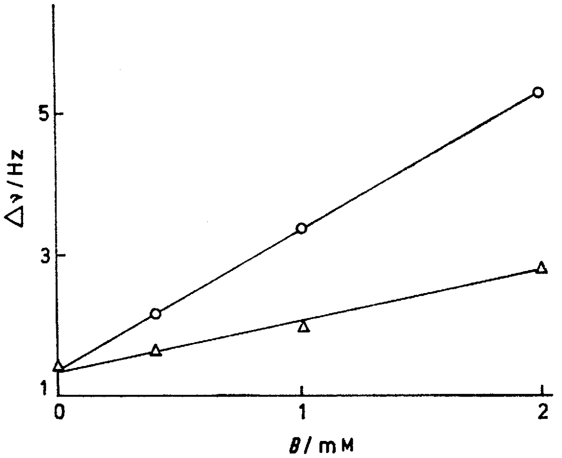

FIGURE 1 Linewidths of proton signals of CH_3 (lower) and CH_2 (upper) in propionate (A = 680 mM) as a function of total copper(II) ion concentration B in aqueous solution at 34·2 °C. (Chemical shifts = 1·04 and 2·19 p.p.m., respectively)

TABLE 2

Relative proton relaxation rates (s^{-1}) for halogenocarboxylates

	A/mM	$10^{-3}\bar{n}/T_2$	$10^{-3}\bar{n}/T_3$	$10^{-3}\bar{n}/T_4$
Chloroacetate	710	1·2		
Bromoacetate	690	1·8		
Dichloroacetate	770	1·1		
2-Bromopropionate	540	3·8	0·9	
2,2-Dichloropropionate	620		0·38	
3-Chloropropionate	620	4·0	3·0	
2-Bromobutyrate	540	5·2	1·8	0·37
2-Bromoisobutyrate	600		0·68	
3-Chlorobutyrate	630	4·4	2·0	1·1
4-Chlorobutyrate	640			1·4

4-*Hydroxycarboxylates and* 3-*Alkoxycarboxylates*.—These also follow the sequence found for unsubstituted carboxylates. The results obtained are given in Table 3. Measurements were not possible on the 3-methylene group of 4-hydroxyvalerate, owing to partial overlapping of the multiplets and spin–spin coupling with the two adjacent groups; * nor could the 3- and 5-CH_2 signals of 3-ethoxypropionate be resolved. Hence these ligands, which have a second potential donor group, appear to form predominantly non-chelated copper(II) complexes in solution. The n.m.r. measurements do not eliminate the possibility of some chelated species being present, since the peaks observed are weighted averages for all the forms in which the ligand is present. A small proportion of chelates might therefore have little effect on the broadening sequence.

2-*Alkoxycarboxylates and* 3-*Hydroxycarboxylates*.—These systems depart from the pattern of behaviour described above. The effects of increasing copper(II) ion concentration B on the methoxyacetate spectrum is shown in Figure 2. The methyl resonance is broadened more than that of the methylene signal, as shown by its greater decrease in height. Similarly, with ethoxyacetate, the values of $\bar{n}/T_i$ decrease in the order 4-CH_2 > 2-CH_2 > CH_3, see Table 4.

TABLE 3

Relative proton relaxation rates (s^{-1}) for 4-hydroxy- and 3-alkoxy-carboxylates

	A/mM	$\frac{10^{-3}\bar{n}}{T_2}$	$\frac{10^{-3}\bar{n}}{T_3}$	$\frac{10^{-3}\bar{n}}{T_4}$	$\frac{10^{-3}\bar{n}}{T_5}$	$\frac{10^{-3}\bar{n}}{T_6}$
4-Hydroxybutyrate	555	4·6	3·8	1·9		
4-Hydroxyvalerate	500	5·2		2·9	0·74	
3-Methoxypropionate	630	2·7	1·0		0·17	
3-Ethoxypropionate	510	1·8				0·069

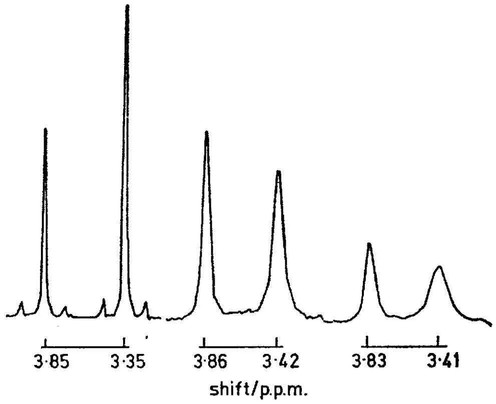

FIGURE 2 Proton magnetic resonance spectra of methoxyacetate (A = 620 mM) for B = 0, 1·01, and 1·91 mM (from left to right) in D_2O solution at 34·2 °C

TABLE 4

Relative proton relaxation rates (s^{-1}) for 2-alkoxy- and 3-hydroxy-carboxylates

	A/mM	$\frac{10^{-3}\bar{n}}{T_2}$	$\frac{10^{-3}\bar{n}}{T_3}$	$\frac{10^{-3}\bar{n}}{T_4}$	$\frac{10^{-3}\bar{n}}{T_5}$
Methoxyacetate	620	2·8		6·7	
Ethoxyacetate	590	5·0		18·5	4·2
3-Hydroxypropionate	630	2·8	15		
3-Hydroxybutyrate	620	5·8	110	3·5	

The effect of varying copper(II) concentrations on the spectrum of 3-hydroxypropionate is shown in Figure 3. The relaxation time of the 3-CH_2-triplet is clearly shortened more than that of the 2-CH_2-triplet by addition of copper(II), as shown by the greater reduction in height and partial collapse of the multiplet structure of the former resonance. The values of $\bar{n}/T_i$ for 3-hydroxybutyrate decrease in the order CH > CH_2 > CH_3, as

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* Subsequent use of a Dupont curve analyser has proved effective; [27] alternatively, the resonances may be separated by employing a pseudo-contact shift lanthanide cation [27,30] at constant concentration in competitive equilibrium with the copper ions.

shown in Table 4 and again the paramagnetic ion has the greatest effect on the group in the 3-position.

Hence the protons of the group in the 4-position relative to the carboxy-group have the smallest value of T_i in the 2-alkoxycarboxylato-complexes. Similarly, for the 3-hydroxycarboxylates, the protons attached to the 3-carbon have the smallest value of T_i. These results indicate that chelation takes place in solution to form five- and six-membered rings respectively. This conclusion applies whether or not scalar coupling takes place. The complexes are not necessarily 100% chelated in solution, since a small proportion of non-chelated species would probably have little effect on the values of T_i. For a six-membered ring, the group in the 3-position would be expected to be closer to the metal than the group in the 2-position, thus explaining the observed sequence. An alkyl group projecting from an ether oxygen atom in a five-membered ring may adopt a preferred conformation, which brings the 4-position protons closer on average to the metal ion than the 2-position protons, and thus account for the greater relaxation of the former resonance. Alternatively, or additionally, if scalar coupling contributes to the relaxation, a greater transference of unpaired electron density may take place to the protons in the 4-position. We have shown that, in the solid state, copper(II) methoxyacetate[6] and ethoxyacetate[7] dihydrates are both indeed chelates, with the organic ligands *trans* and planar. The ratio $T_4(CH_3)/T_2(CH_2) = 2{\cdot}39$ obtained in this work for methoxyacetate corresponds to a ratio of the sixth powers of the mean distances from the protons to the central copper(II) ion of 2·23, calculated from our crystal structure[6] (*i.e.* on the assumption that the relaxation is dominated by the dipolar term). Alternatively, the ratio of the distances = 1·16, calculated from the present results, corresponds to a ratio of $1{\cdot}14_3$, calculated from the crystal structure. Hence, the 2-alkoxycarboxylates do appear to be bidentate in solution and moreover, the dimensions of the complex appear to be remarkably similar both in the solid state and in solution. The observed sequences of values of T_i for the 2-alkoxy- and 3-hydroxy-carboxylates would also result if the copper were attached to the hydroxy or ether oxygen atom alone and not to the carboxy, *i.e.* with the ligand unidentate. This type of co-ordination is most improbable on electrostatic grounds. It is more likely that the ligand becomes comparatively firmly attached to the metal by the carboxylate group and that an equilibrium is then established in solution between chelated species (with the oxygen of the substituent co-ordinated) and non-chelated species. This equilibrium favours the chelated form for the 2-alkoxy- and 3-hydroxy-carboxylates, but favours the non-chelated form for 3-alkoxy and 4-hydroxy-carboxylates.

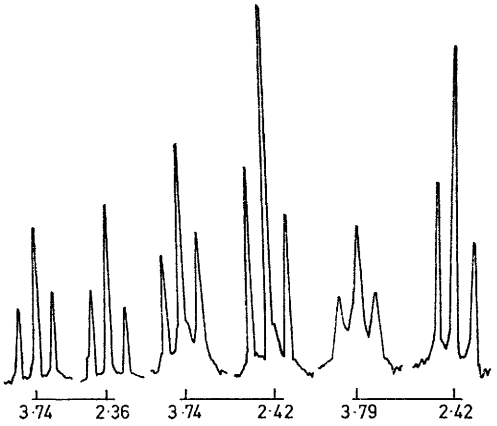

FIGURE 3 Proton magnetic resonance spectra of 3-hydroxypropionate (A = 630 mM) for B = 0, 0·14, and 0·285 mM (from left to right) in D_2O solution at 34·2 °C. The left and right hand triplets of each pair refer to the 3-CH_2 and 2-CH_2 protons respectively

2-Hydroxycarboxylates.—These ligands would be expected to follow the sequence found for unsubstituted carboxylates owing to the distance dependence, whether or not a co-ordinate bond is formed with the hydroxy oxygen atom. The results in Table 5 show that values of $\bar{n}/T_i$ are very much larger for the resonances in a 2-hydroxycarboxylate than for the corresponding resonances in its halogen analogue (see also Figure 4). The

TABLE 5

Relative proton relaxation rates (s^{-1}) for 2-hydroxycarboxylates and their unidentate analogues

	A/mM	$10^{-3}\bar{n}/T_2$	$10^{-3}\bar{n}/T_3$	$10^{-3}\bar{n}/T_4$
Glycollate	710	70		
Chloroacetate	710	1·2		
Bromoacetate	690	1·8		
Glyoxylate	530	57		
Dichloroacetate	770	1·1		
Lactate	560	68	30	
2-Bromopropionate	540	3·8	0·9	
2-Hydroxybutyrate	560	52	27	3·3
2-Bromobutyrate	540	5·2	1·8	0·37
2-Hydroxyisobutyrate	600		20	
2-Bromoisobutyrate	600		0·68	
Mandelate	430	21		1·3 *
Phenylacetate	100	1·2		0·28 *

* Average over 2-, 3-, and 4-ring positions.

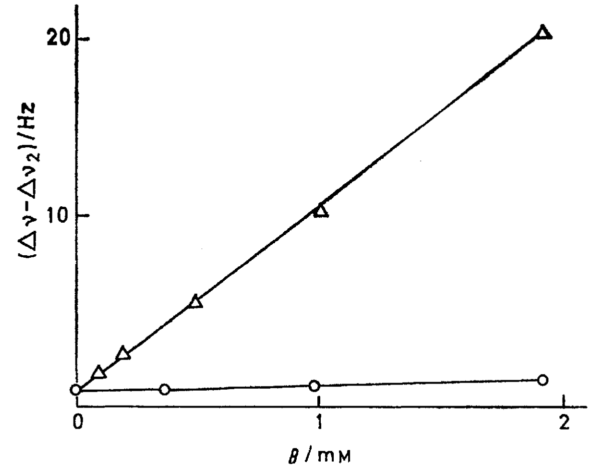

FIGURE 4 Linewidths of proton signals of 2-hydroxyisobutyrate (upper) and 2-bromoisobutyrate (lower) as a function of total copper(II) ion concentration B in aqueous solution at 34·2 °C. (Chemical shifts = 8·63 and 8·12 p.p.m. respectively)

spectra, however, are of identical spin–spin multiplicity and the electronic effects of the substituents are similar, as shown by the decrease in pK_a and downfield chemical shifts compared with the unsubstituted compounds.

The results in Table 5 show that the value of $\bar{n}/T_i$ for the 2-position protons is at least 10 times larger in a 2-hydroxycarboxylate than in its halogeno-analogue. The differences cannot be explained by variations in $\bar{n}$ alone, as shown above (p. 1007), but are consistent with chelation by the 2-hydroxycarboxylates. The same conclusion is reached for mandelate from a comparison of the values of $\bar{n}/T_i$ and $\bar{n}$ with those of phenylacetate. (The solubility of the bromo-analogue of mandelate was too low for n.m.r. studies.) Chelation will increase the dipolar contribution to the relaxation by decreasing the distance between the protons attached to the 2-carbon and the metal, and may also increase the scalar coupling contribution by providing an additional point of contact between metal and ligand. In lactate, 2-hydroxybutyrate and 2-hydroxyisobutyrate, $\bar{n}/T_3$ (for the 3-position protons) is at least 15 times greater than in the analogous halogeno-system, also in accordance with a chelated structure. The ratio of $\bar{n}/T_4$ for the methyl group of the 2-hydroxybutyrate to that of the 2-bromobutyrate is approximately 9 : 1, and the mean $\bar{n}/T_i$ ratio for the phenyl groups of mandelate and phenylacetate is approximately 5 : 1, indicating that the effects become less marked as the distances from the potential binding sites and from the metal ion increase. The ratios are still larger than the expected $\bar{n}$ ratios, however.

It is likely that the higher values of $\bar{n}/T_i$ for analogous protons in 2-hydroxy- and 2-halogeno-carboxylates are due, at least in part, to a restriction in free rotation[30a] of the carbon atoms which bear those protons. This locking of protons into preferred positions would be a consequence of chelation.

An alternative source of increased relaxation in a hydroxycarboxylate could be a slow exchange of the hydroxyl proton with solvent, giving a contribution from τ_B in equation (3) to the observed linewidth. Exchange broadening is extremely unlikely, however, since exchange is always so rapid that no separate signal can be observed for the hydroxy-proton. Furthermore, such exchange broadening would also be possible for the protons attached to the 4-position carbon in copper(II)–4-hydroxycarboxylate systems, and for solutions of the ligands themselves in the absence of copper(II). The experimental data show no abnormal broadening in either case. The crystal structures of copper(II) glycollate, copper(II) lactate monohydrate, and copper(II) 2-hydroxyisobutyrate dihydrate have been determined,[6] and in each case the ligand is bidentate in the solid.

Other Monocarboxylate Systems.—The cyanoacetate, phenylacetate, phenoxyacetate, and *p*-hydroxyphenoxyacetate systems have also been studied (see Table 6). The aromatic proton signals of phenoxyacetate have a complex splitting pattern caused by the non-equivalence of the ring positions and linewidths have not been measured. For *p*-hydroxyphenoxyacetate, the value of $\bar{n}/T_i$ for the aromatic protons, which are equivalent, represents an average over the 2- and 3-ring positions.

TABLE 6

Relative proton relaxation rates (s^{-1}) for some miscellaneous monocarboxylates

	A/mM	$10^{-3}\bar{n}/T_2$	$10^{-3}\bar{n}/T_i$ *
Cyanoacetate	930	1·0	
Phenoxyacetate	406	4·7	
p-Hydroxyphenoxyacetate	470	5·4	1·9
Phenylacetate	100	1·2	0·28

* Average for phenyl ring.

Cyanoacetate has a value of $\bar{n}/T_2$ of comparable magnitude to those of chloroacetate and dichloroacetate and compatible with unidentate co-ordination by the ligand. The conclusion that the cyano-group, which is a potential donor, does not co-ordinate copper(II) in solution is also supported by the thermodynamic data.[4] It is also of interest that magnetic[8] and e.s.r.[31] evidence both indicate that the cyanoacetate has a dimeric acetate-type structure in the solid state.

A comparison of the values of $\bar{n}/T_2$ and $\bar{n}$ for phenoxyacetate and *p*-hydroxyphenoxyacetate with those for cyanoacetate and chloroacetate indicates that T_2 is shorter for the 2-aryloxy-systems. This effect could be due to ring formation, as in the 2-alkoxycarboxylate systems. The enhancement of stability for phenoxyacetate is much less marked than for methoxyacetate or ethoxyacetate, but there may be steric hindrance to ring formation by the bulky phenyl group. The value of $\bar{n}/T_i$ is larger for the aromatic protons of *p*-hydroxyphenoxyacetate than for those of mandelate, which was concluded to be mainly bidentate towards copper(II). The aromatic proton signal of the substituted phenoxyacetate, which is an average over the 2- and 3-ring positions, would be expected to be broadened slightly more than the mandelate signal, which is an average over the 2-, 3-, and 4-ring positions, if the ligands were both bidentate. A smaller value of $\bar{n}/T_i$ than for mandelate would be expected for unidentate co-ordination. It is therefore concluded that at least some chelated species are present in the substituted phenoxyacetate solutions. The crystal structure of copper(II) phenoxyacetate dihydrate[6] shows that the ligand is bidentate in the solid, but with a long (*ca.* 2·47 Å) Cu–O contact to the ethereal oxygen atom. On the other hand, the ligand is only unidentate[32] in crystalline copper(II) phenoxyacetate trihydrate. It is therefore more than likely that the equilibrium cyclic complex $\rightleftharpoons$ acyclic complex is rather evenly balanced in solution.

Dicarboxylates.—The results obtained for the unsubstituted ligands, malonate and succinate and for the

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[30] (*a*) M. R. Harrison, B. E. Moulds, and F. J. Rossotti, *Trans. Royal Inst. Technol.*, 1972, **268**, 263; 'Contributions to Co-ordination Chemistry in Solution,' ed. E. Högfeldt, Swedish Nat. Sci. Res. Council, Stockholm, 1972; (*b*) M. R. Harrison and F. J. C. Rossotti, unpublished work; M. R. Harrison, D.Phil. Thesis, Oxford University, 1970.

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[32] C. V. Goebel and R. J. Doedens, *Chem. Comm.*, 1970, 839.

substituted dicarboxylates, 2-methylmalate and diglycollate, are recorded in Table 7. The spectra of diglycollate and succinate are singlets, since the protons in these ligands are all equivalent. The methylene hydrogen atoms in 2-methylmalate are non-equivalent owing to the presence of an asymmetric carbon atom and give separate signals. The $\bar{n}/T_2$ values are, however, very similar for both resonances.

TABLE 7

Relative proton relaxation rates (s^{-1}) for dicarboxylates

	A/mM	$10^{-3}\bar{n}/T_2$	$10^{-3}\bar{n}/T_3$
Malonate	570	23	
Succinate	510	4·1	
Citramalate	510	12, 13 *	12
Diglycollate	268	4·0	

* See text.

Malonate appears to be a bidentate ligand from the thermodynamic data.[3,33] The value of 23×10^3 s^{-1} for $\bar{n}/T_2$ is in full agreement with this conclusion, being appreciably larger than that for the methylene group in the unidentate ligand propionate. The $\bar{n}/T_2$ value for succinate is comparable with the values found for 2-position protons in unsubstituted carboxylates (Table 1). Succinate would be expected to have a greater tendency to form a seven-membered ring than a 4-hydroxymonocarboxylate from electrostatic considerations. If both carboxy-groups were co-ordinated, the average distance of each CH_2 group from the metal ion would be similar to that of the 2-CH_2 group in propionate. If one carboxy group alone were co-ordinated, the distance from copper(II) of the protons of the 3-CH_2 group would approximately equal the distance of the 3-CH_2 protons in butyrate from bound copper(II) and a value of T_2 intermediate between T_2 and T_3 for butyrate would thus be expected. In our solutions, values of $\bar{n}$ were approximately equal for butyrate and malonate, and somewhat lower for succinate. Hence, T_2 for succinate is probably shorter than T_2 for butyrate, and the n.m.r. data are consistent with bidentate co-ordination, although the possibility of unidentate species also occurring in solution cannot be discounted.

2-Methylmalate has three possible co-ordination sites (two carboxys and the hydroxy). Values of $\bar{n}/T_i$ for the methyl and the non-equivalent hydrogens of the CH_2 group are all similar, and are larger than the value for succinate. The ligand is therefore presumed to be at least bidentate. The most probable bidentate structure involves co-ordination by the hydroxy-group and the adjacent carboxy, to give a five-membered ring. A Dreiding model of the complex indicated that the second carboxy could also occupy an axial binding site, although a longer bond would probably result giving a tetragonally distorted octahedral structure. However, in the solid state, such additional co-ordination does not occur with the related tartrate ligand. Our *X*-ray diffraction studies[34] show that each half of the tartrate ion acts as a bidentate ligand towards a different copper(II) ion, resulting in the formation of a dimer with +-tartrate and chains with *meso*-tartrate, *cf.* the structure of the dimeric anionic complex containing both (+)- and (−)-tartrate (R. J. Missavage, R. L. Belford, and I. C. Paul, *J. Co-ordination Chem.*, 1972, **2**, 145).

For diglycollate and succinate, $\bar{n} \sim 1$ and the values of $\bar{n}/T_2$ are similar. Hence, diglycollate appears to be bidentate with one free carboxylate group as we, unlike other workers,[35,36] infer from the thermodynamic data.[2] It is clear from the crystal structures of the lanthanide compounds[37] $Na_3[Ln(O_2CCH_2OCH_2CO_2)_3],NaClO_4,6H_2O$ that diglycollate is planar and could only be tridentate towards copper(II) with a gross distortion of the co-ordination polyhedron of the cation.

Anisotropic g Tensor and Scalar Contributions.—The appropriate equations for nuclear relaxation induced by paramagnetic metal ions having anisotropic *g* factors were derived by Sternlicht.[38] These are so cumbersome that they are not reproduced here in the interests of brevity. The *g* factors of copper(II) complexes with oxygen-donor ligands of the type under consideration in the present work are insensitive[1] to the precise nature of the ligand. Accordingly the relative magnitudes of the several terms in Sternlicht's equations contributing to the longitudinal and transverse relaxation rates $1/T_l$ and $1/T_t$ were assessed by setting[1] $g_{\parallel} = 2{\cdot}35$ and $g_{\perp} = 2{\cdot}07$, together with appropriate values of the several other parameters (see below). Terms in $(g_{\parallel} - g_{\perp})$, $\sin^2\theta$ and $\sin^4\theta$ (where θ is the angle between the proton-metal ion vector and the principal axis of the complex) and also the term arising from interference between the electron exchange and dipole–dipole terms were shown to be relatively unimportant throughout. The longitudinal relaxation rate is dominated by the time modulation of the dipole–dipole interaction and the transverse relaxation rate by the same process together with electron exchange (scalar coupling). Finally, and most importantly, the values of $1/T_l$ and $1/T_t$ were found to be within experimental error (a few percent) of those calculated from the appropriate forms of the Solomon–Bloembergen equations,[39] which are valid for isotropic *g* factors. Hence, for each type of proton, we take

$$\frac{1}{T_l} = \frac{2\bar{n}B\gamma^2g^2\beta^2S(S+1)}{15Ar_i^6}\left[3\tau_c + \frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right]$$

and

$$\frac{1}{T_t} = \frac{\bar{n}BS(S+1)}{A}\left\{\frac{\gamma^2g^2\beta^2}{15r_i^6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{\mathscr{A}^2\tau_e}{3\hbar^2}\right\}$$

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[33] G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, Amsterdam, 1966, p. 152.

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where γ is the proton magnetogyric ratio, β the Bohr magneton, S the electron spin quantum number, r_i the distance between the protons on the i-th carbon atom of the ligand and the bound copper(II) ion, τ_c the correlation time for dipolar coupling, ω_S the electronic Larmor angular precession frequency, $\mathscr{A}$ the electron-proton isotropic hyperfine coupling constant, and τ_e the correlation time for spin exchange interaction [averages, where appropriate, *cf.* equation (3)].

The ratio T_1/T_t was obtained by spin-echo methods and found to be 4·4 for both the acetate and 2-hydroxyisobutyrate systems. These values are consistent with appreciable contributions of both the dipolar and spin-exchange terms to $1/T_t$. The magnitudes of the separate contributions for the acetate system were determined by measuring T_1 and T_t as functions of temperature at two frequencies (20 and 35 MHz).

The frequency dependence of the relaxation times over the range of temperatures ($279 \leqslant K \leqslant 315$) common to both frequencies indicated that $\omega_S\tau_c \sim 1$. Use of this value enabled the correlation times calculated for the two frequencies to be fitted to the same linear function of reciprocal temperature (see Figure 5) from which an activation energy of 30·8 kJ mol^{-1} was obtained for the correlation time and hence the tumbling of the complex in solution (see below).

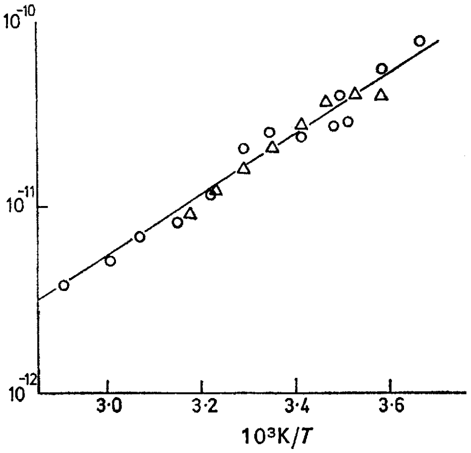

FIGURE 5 Dipolar correlation times τ_c of $(CH_3CO_2)_2Cu(H_2O)_4$ (A = 2000 mM, B = 12·0 mM, $\bar{n}$ = 2·0) determined at 20 MHz (○) and 35 MHz (△) plotted as a function of reciprocal temperature

Cox and Morgan[40,41] have calculated activation energies (*i.e.* effective barriers to tumbling) of 21·2, 18·8, and 16·2 kJ mol^{-1} for the ions $[Cu(H_2O)_6]^{2+}$, $[Cu(en)(H_2O)_4]^{2+}$, and $[Cu(en)_2(H_2O)_2]^{2+}$ respectively. Cox[42] also found that the activation energies increased with the size of bisdiaminecopper(II) complexes. Our value of 30·8 kJ mol^{-1} for $(CH_3CO_2)_2Cu(H_2O)_4$, which is the predominant complex under the experimental conditions ($\bar{n} \sim 2$), is therefore reasonable, as the bisacetatotetraquo-species must be larger than the hexa-aquocopper(II) ion, *cf.* ref. 43.

No contact shifts were observed in any of the carboxylato-systems under the conditions used ($A \gg B$). In some systems, small downfield shifts were noticed with increasing copper(II) ion concentration. However, these were seldom larger than the experimental reproducibility and may have been at least partly caused by small changes in pH, which are known to affect the chemical shifts.[44,45] Accordingly, it was only possible to deduce that $(\mathscr{A}\hbar)^2 \leqslant 10^{11}$ rad s^{-1} for the acetate system. This value is to be compared with that of $1{\cdot}4 \times 10^{11}$ rad s^{-1} for the hexa-aquocopper(II) ion.[46] Correlation times for T_1 were calculated as a function of temperature by setting the effective magnetic moment, $g^2\beta^2S(S+1) = 2{\cdot}0$ B.M. and $r = 4{\cdot}6$ Å, the latter value being based upon bond lengths and angles in the crystalline acetate monohydrate[47] and other carboxylatocopper(II) complexes.[6] These parameters were used to calculate the dipolar contribution to T_t, whence lower limits of $\tau_e \sim 10^{-8}$ s were obtained as a function of temperature. These last values were of the same order of magnitude as the electron spin-lattice relaxation time τ_S estimated from solution e.s.r. spectra. Values of $\tau_e = \tau_S \sim 10^{-8}$ s have previously been assumed for the bisethylenediaminecopper(II) ion.[41]

The spin-exchange interaction may be interrupted by both electron spin relaxation and chemical exchange. The rates are additive so that:

$$\frac{1}{\tau_e} = \frac{1}{\tau_S} + \frac{1}{\tau_B}$$

As we were unable to obtain a precise value of τ_S owing to hyperfine splitting, the relative contributions of τ_S and τ_B to τ_e could not be distinguished. The dipolar interaction is interrupted by the same two processes, but in addition the coupling may be modulated by rotation of the complexes. Hence,

$$\frac{1}{\tau_c} = \frac{1}{\tau_S} + \frac{1}{\tau_B} + \frac{1}{\tau_r}$$

where the rotational correlation time τ_r describes the movement of the proton–metal ion vector in space, as the complexes tumble in solution. This last term causes the most rapid fluctuation in the energy of interaction by 3 orders of magnitude so that:

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} \sim 10^{11}\ \text{s}^{-1}$$

This value is close to that of 5×10^{10} s^{-1} reported[40] for the hexa-aquocopper(II) ion.

Finally, we turn to an assessment of the dipolar and electron exchange contributions to the spin–spin

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[41] P. F. Cox and L. O. Morgan, *J. Amer. Chem. Soc.*, 1959, **81**, 6409.

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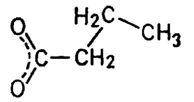
relaxation rates. Using the parameters obtained above, for the bisacetatocopper(II) complex, we calculate a 25% dipolar and 75% scalar contribution to the proton relaxation rate. This somewhat surprisingly high scalar contribution must fall off sharply for protons on carbon atoms C_i ($i > 2$) in longer chain unidentate carboxylate ligands, since the vicinal interproton coupling constant $|^3J_{HH}| > |^4J_{HH}|$ by factors of about 4 to 20.[48-52] However, this marked fall off with increasing i will not occur in bidentate ligands.

In the absence of further spin-echo measurements, we assess the fall off of the scalar component in bisbutyratocopper(II) by an alternative method. We have already[30a] reported the relaxation rates for the several protons in the analogous gadolinium(III) system, where we can validly assume the absence of a scalar component. The ratios r_{i+1}/r_i were calculated from the values of $1/T_i$ and normalised on the crystallographic RCO_2–Gd bond length of 2·41 Å.[37] These values, incidentally, imply a distinctly compact conformation for the butyratogadolinium(III) complexes. On the not unreasonable assumption that the copper(II) complexes have a similar conformation in solution, the several r_{i+1}/r_i were calculated, using our mean crystallographic RCO_2–Cu bond length[6] of 1·92 ± 0·02 Å. On the further assumption that the dipolar contribution for protons on carbon atom C(2) is 25% in the butyrate, as in the acetate, the dipolar and scalar contributions to the spin–spin proton relaxation rates on carbon atoms C(3) and C(4) in bisbutyratocopper(II) were calculated by using the values of $1/T_i$ in Table 1. The relative magnitudes given in Table 8 are independent of the value of $\bar{n}$ used, although the absolute rates do depend on the value $\bar{n} = 2·00$ used in the calculation. The relative contributions are, of course, sensitive to our choice of r_i. If r_3 and r_4 were 5·3 and 6·9 Å respectively, rather than the values given in Table 8 (*i.e.* corresponding to an extended conformation rather than the compact conformation implied by the relaxation rates in the gadolinium system) then the dipolar contributions to the relaxation rates of protons on carbon atoms C(3) and C(4) would be 75 and 92% respectively rather than the 57 and 85% contributions given in Table 8. It is of interest that the dipolar component of the proton spin–spin relaxation times increases to 85% for protons on carbon atom C(4), and that the scalar component falls off by factors of from 5 to 8. These last are reasonable values for electron transmitted energy couplings along a saturated carbon chain.



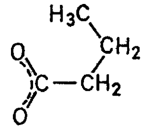


TABLE 8

Dipolar and scalar contributions to transverse relaxation rates (s^{-1}) of protons in bisbutyratocopper(II)

	r_i/Å	Dipolar	Scalar	Total
$H_2C(2)$	4·60	550	1650	2200
$H_2C(3)$	4·79	430	320	750
$H_3C(4)$	5·39	212	38	250

CONCLUSIONS

The main deductions made from our n.m.r. studies about the structures of copper(II) complexes with potentially multidentate ligands are that 2-hydroxy-, 2-alkoxy-, and 3-hydroxy-monocarboxylates are predominantly bidentate towards copper(II) in aqueous or D_2O solution, but that 3-alkoxy- and 4-hydroxy-carboxylates are mainly unidentate. Some supporting evidence for chelation in 2-hydroxy- and 2-alkoxy-systems may be adduced from calorimetric measurements,[5] i.r. spectroscopy of D_2O solutions,[53-55] for the lactate system also from optical rotatory dispersion and circular dichroism,[56,57] and from our determinations of hydration numbers in solution.[43,30b,]

Preferential co-ordination of 3-hydroxy-groups to copper(II) as compared to 3-alkoxy-groups is not altogether unexpected in view of the differences between the stability constants.[4] Even for the 2-substituted ligands, differences in the ligational enthalpies[5] and, in the solid state, differences between the Cu–OH and Cu–OR bond lengths,[6,7] the molecular g values,[1] and the electronic spectra[1] of the complexes all indicate that the Cu–OH bond is stronger than the Cu–OR bond. Intramolecular hydrogen bonding occurs in dilute carbon tetrachloride solutions of 2-alkoxy-acids but not of 3-alkoxy-acids.[58] This difference, which has been attributed[59] to the unfavourable conformation required for formation of the six-membered ring, parallels the difference in structure deduced for the corresponding copper(II) complexes in D_2O.

Scalar and dipolar contributions to the spin–spin relaxation rates of protons on vicinal carbon atoms in saturated chains have been assessed. Although the scalar effect is surprisingly high for protons on carbon atom C(2), it falls off sharply through C(3) to C(4).

We thank Mrs. E. E. Richards for recording the room temperature n.m.r. spectra, Dr. D. J. Bell for the variable temperature spin-echo measurements on the acetate system, and the S.R.C. for a research studentship to K. B. D.

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