

Proton Magnetic Resonance Study of the Solvation of Copper(II) Acetate Dimeric Molecules in Ethanol/Acetic Acid Mixtures

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NMR line width and line shift of the hydroxyl and acetic acid methyl solvent protons in ethanol/acetic acid solutions of copper acetate have been measured between -100°C and $+100^{\circ}\text{C}$. The results indicate a selective solvation of acetic acid on the axial positions of the copper acetate dimeric molecules. The CH_3 and OH axial ligand protons exchange between solvated and bulk acetic acid at the same rate characterized by: rate constant $1/\tau_M = 2.5 \times 10^4 \text{ s}^{-1}$ at 25°C , and activation energy $\Delta H = 10.7 \text{ kcal/mol}$. The exchange reaction is assumed to be of the first order. The hyperfine interaction constant for the ligand methyl protons is $A/h = 1.07 \times 10^6 \text{ Hz}$. The electron spin relaxation time τ_s is estimated to be $2.6 \times 10^{-10} \text{ s}$ at 25°C , provided the correlation time for the complex $\tau_c = 10^{-10} \text{ s}$. A coordination number of one was assumed in the calculations.

At low temperature, evidence is seen for one extra ligand per Cu atom, probably hydrogen-bonded to the carboxyl oxygen opposite to the hydrogen bond formed by the axial ligand. The chemical exchange rate constant for this is 230 s^{-1} at -67°C .

The hydroxyl proton transfer between EtOH and HAc in solution goes fast compared to ligand exchange at temperatures below $+50^{\circ}\text{C}$.

In previous work ^{1,2} (hereafter referred to as I and II) we have shown that copper(II) acetate persists mainly as dimeric molecules $\text{Cu}_2(\text{CH}_3\text{COO})_4$ in acetic acid and ethanol solutions. The degree of dissociation to monomeric molecules is very small in acetic acid, and addition of HAc to ethanol solutions of copper acetate stabilizes the dimeric molecules to a high extent. We have proposed ² that the dimers are stabilized by acetic acid coordination to the axial ligand positions. The PMR results to be reported here support this assumption.

Parameters characterizing the ligand chemical exchange reaction, and the magnetic dipolar and hyperfine interaction between the HAc ligand protons and the unpaired electrons of the dimeric copper acetate molecule, Cu_2AC_4 , have been derived using NMR line broadening technique.³ The large tempera-

ture variation allowed by the solvent mixtures results in an approximately 10^7 -fold change in the axial ligand exchange rate. In the low temperature region, the formation of another more weakly bound HAc ligand is reflected in the broadening of the HAc methyl proton signal.

EXPERIMENTAL

All the PMR spectra were recorded with a Varian A-60 A spectrometer equipped with a V-6040 variable temperature controller. The temperature was determined by measurement of the peak separation in ethylene glycol and methanol, and was measured and controlled to within $\pm 2^\circ\text{C}$. One vol% TMS was used as an internal standard for the line shift measurements. The temperature was varied between -100°C and $+100^\circ\text{C}$.

Solutions were prepared by dissolving hydrated copper acetate in previously mixed EtOH and HAc in given volume percentage ratios. The copper concentrations given are based on the monomeric formula, CuAc_2 . Two sets of solutions were made up and measured. They were identical, except that one contained CuAc_2 . The PMR line shift and line width contributions, due to hyperfine and dipolar interaction with the paramagnetic species, were measured as the difference of the peak frequencies and widths in the two solutions. A positive frequency shift means that the line is shifted downfield. Care was taken to keep the r.f. level low enough to avoid saturation. Samples used for measurements were always less than two days old.

Fig. 1 shows PMR spectra of ethanol solutions of CuAc_2 with successive addition of acetic acid. The ethanol ethyl group stays nearly constant, while the appearing HAc methyl signal is very broad and shifted downfield, indicating a strong interaction with the copper species present.

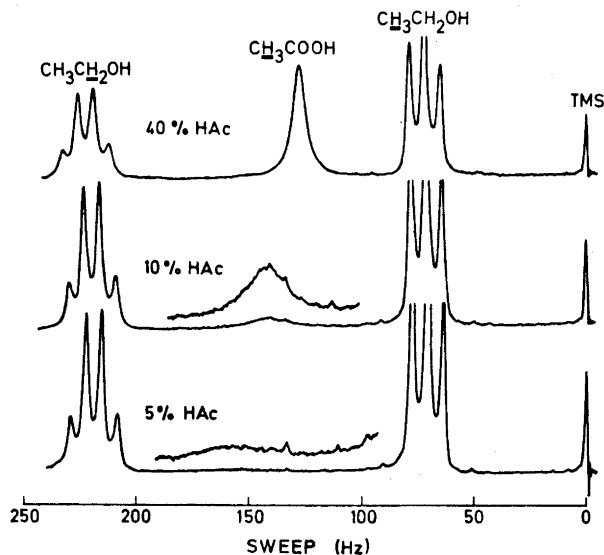


Fig. 1. EtOH ethyl and HAc methyl lines at 40°C in PMR spectra of EtOH solutions of CuAc_2 with successive addition of HAc. $c_{\text{CuAc}_2} = 0.33 \text{ mol/l}$.

No separate peaks were observed belonging to HAc molecules coordinated to dimeric copper acetate. The observed lines corresponded either to free solvent molecules or to an average of free and bound solvent molecules, depending on the exchange rate.

The precision of the measured line shifts and line widths are about $\pm 10\%$.

In one set of samples, the water content was increased to about 0.57 M, in order to detect its effect on the exchange rate.

The materials used were the same as described in II.

THEORY

The acetic acid molecules can be in either of two environments: in the free solvent or in the coordination shell of the dimeric Cu_2Ac_4 molecule, designated with the indices A and M, respectively. The HAc solvent protons can exchange between A and M at a rate characterized by the average residence time of a HAc molecule in the M environment, τ_M .

In the coordination shell, the dipolar and hyperfine interaction of the nuclei with the unpaired electrons result in rapid nuclear relaxation, and a very broad PMR line shifted downfield. The antiferromagnetic coupling between the two copper atoms in the dimeric molecules results in a non-magnetic singlet ground state, and a magnetic triplet state some 300 cm^{-1} higher in energy.⁴ Only the magnetic triplet state serves as an effective relaxation center for the attached ligand protons. The relaxation between triplet and singlet states within a dimeric molecule probably goes fast, compared to ligand exchange. Hence, the ligand protons are exposed to an average of triplet and singlet relaxation efficiencies. The Solomon-Bloembergen^{5,6} equation for the transverse relaxation rate of nuclei bound to a paramagnetic ion, and the Bloembergen⁷ equation for the contact shift of these nuclei, can be modified to give a singlet-triplet averaged effective relaxation rate $1/T_{2M}$ and an effective contact shift $(\Delta\omega_M)_c$ of nuclei bound to a copper dimeric molecule. Following the procedure in I, treating the dimer in terms of two spins $S = 1/2$, and taking into account that the rotation correlation time τ_c and the electron spin relaxation time τ_s are short, compared to the inverse of the proton frequency ($1/\omega_I$), and long, compared to the inverse of the electron spin precession frequency ($1/\omega_S$), the formulas are (it is assumed that $\tau_c < \tau_s$):

$$\frac{1}{T_{2M}} = \frac{7}{15} \frac{\hbar^2 \gamma_I^2 \gamma_S^2 S(S+1) \tau_c}{r^6} \frac{[2(1+x)^2 + (1-x)^2]}{[3 + \exp(\Delta/kT)]} + \frac{1}{3} S(S+1) \left(\frac{A}{\hbar}\right)^2 \tau_s \frac{\chi_d}{\chi_m} \quad (1)$$

$$\left(\frac{\Delta\omega_M}{\omega}\right)_c = \frac{\gamma_S}{\gamma_I} \frac{S(S+1)A}{3kT} \frac{\chi_d}{\chi_m} \quad (2)$$

The dimer/monomer susceptibility ratio is $\chi_d/\chi_m = 4/[3 + \exp(\Delta/kT)] \approx 0.52$ at 25°C from eqn. (1) in II. Δ is the singlet-triplet energy separation, x the ratio of the dipolar fields from the two dimer spins at the ligand proton position, and r the distance from the ligand proton to the adjacent Cu atom in the dimer.

The dimer triplet probably has an anisotropy in the g -factor of the same order of magnitude as in copper acetate crystals,⁴ where $g_{\parallel} - g_{\perp} = 0.34$, and a contribution to the shift dipolar in origin, must be considered.⁸ If a nucleus is attached to the paramagnetic molecule at a distance r from the unpaired

electrons, and the vector \vec{r} makes an angle ψ with the molecular symmetry axis, and if the molecular motion correlation time is such that $1/\tau_s \ll 1/\tau_c \ll |g_{\parallel} - g_{\perp}| \beta H \hbar^{-1}$, the additional dipolar shift is given by⁹

$$\left(\frac{\Delta\omega_{\mathbf{M}}}{\omega}\right)_{\text{dip}} = \frac{\beta^2 S(S+1)}{3kT} \frac{(3\cos^2\psi - 1)}{r^3} \left[\frac{1}{2g_{\parallel}} + \frac{g_{\perp}^2}{2(g_{\parallel}^2 - g_{\perp}^2)^{1/2}} \cos h^{-1}\left(\frac{g_{\parallel}}{g_{\perp}}\right) \right] \\ \left[\frac{2g_{\parallel}^3 + g_{\parallel}g_{\perp}^2}{4(g_{\parallel}^2 - g_{\perp}^2)} + \frac{g_{\perp}^4 - g_{\perp}^2g_{\parallel}^2}{4(g_{\parallel}^2 - g_{\perp}^2)^{3/2}} \cos h^{-1}\left(\frac{g_{\parallel}}{g_{\perp}}\right) \right] K \quad (3)$$

K is a correction factor for the antiferromagnetic coupling effect of the same order of magnitude as χ_d/χ_m , which applies for the contact shift (eqn. (2)). However, K has not been worked out in detail, because the dipolar shift appears to be small and enters the problem as a correction only.

Two processes contribute to the relaxation rate in the free solvent. $1/T_{2A} = 1/T_{2A}'' + 1/T_{20}$. $1/T_{2A}''$ is due to dipolar interaction between paramagnetic molecules and solvent protons beyond the coordination shell. It is proportional to the copper concentration, c_{CuAc_2} , and the temperature dependence is given by the dipolar term in eqn. (1)

$$1/T_{2A}'' = \text{const. } c_{\text{CuAc}_2} \tau_c / [3 + \exp(\Delta/kT)] \quad (4)$$

The contribution $1/T_{20}$ due to other relaxation mechanisms is independent of c_{CuAc_2} , and can be deduced from line widths in solvent not containing paramagnetic species.

The very broad and weak coordination shell signal could not be observed directly. But the paramagnetic molecules influence the average PMR line, and we interpret our data, using the formulas derived by Swift and Connick.¹⁰ If the ratio P of M protons to A protons is much less than unity, their equations are

$$1/T_2 = 1/T_{2A} + P \frac{1/T_{2M}(1/T_{2M} + 1/\tau_M) + (\Delta\omega_{\mathbf{M}})^2}{\tau_M(1/T_{2M} + 1/\tau_M)^2 + \tau_M(\Delta\omega_{\mathbf{M}})^2} \quad (5)$$

$$\Delta\omega = P \frac{\Delta\omega_{\mathbf{M}}}{(\tau_M/T_{2M} + 1)^2 + \tau_M^2(\Delta\omega_{\mathbf{M}})^2} \quad (6)$$

Here, $\Delta\omega_{\mathbf{M}} = (\Delta\omega_{\mathbf{M}})_c + (\Delta\omega_{\mathbf{M}})_{\text{dip}}$, $1/T_{2M}$ is defined by eqn. (1), and τ_M is given by¹¹

$$1/\tau_M = (kT/h) \exp(\Delta S/R - \Delta H/RT) \quad (7)$$

where ΔS and ΔH are the entropy and enthalpy of the activation for the chemical exchange reaction.

The total transverse relaxation rate $1/T_2$ is calculated from the experimental PMR line width, using the relation $1/T_2 = \delta\omega/2$, which applies for a Lorentzian line shape, when $\delta\omega/2\pi$ is the full line width in Hz at half maximum.

RESULTS AND DISCUSSIONS

a. Acetic acid methyl proton signal. The effect of CuAc_2 on the NMR signal from the HAc methyl protons in acetic acid/ethanol mixtures is shown in

Fig. 2. HAc methyl PMR line shift (open circles) and line width (filled circles) in ethanol/acetic acid solutions of CuAc_2 as a function of c_{CuAc_2} and $1/c_{\text{HAc}}$.

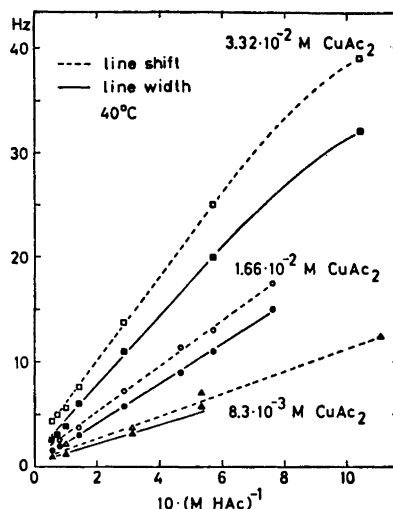


Fig. 2, where the observed line widths and line shifts are plotted *versus* reciprocal HAc concentration. Both the line shift and line width are proportional to c_{CuAc_2} and $1/c_{\text{HAc}}$ to within the experimental errors down to about 1.5 M HAc. The ethanol ethyl group lines are not displaced. Provided the chemical exchange rate is so fast that the signal seen is an average of free and solvated protons, and the nature of the solvated molecules remains constant over the solvent range studied, these results strongly support that HAc ligands are preferred on dimeric molecules in competition with ethanol ligands.

As can be seen from Fig. 3, which gives the temperature variations of the HAc methyl protons line shift in acetic acid/ethanol solutions of CuAc_2 , the averaging is almost complete at 40°C ($10^3/T = 3.2^\circ\text{K}^{-1}$). At low temperatures ($10^3/T > 3.8^\circ\text{K}^{-1}$) the exchange between solvated and bulk acetic acid is too slow to shift the observed bulk peak. Only a very small shift, comparable with shifts in solutions of diamagnetic ions, is observed. It is proportional to c_{CuAc_2} . In the intermediate range in Fig. 3, the measured shifts depend on the exchange rate ($\Delta\omega_{\text{M}}$ and $1/\tau_{\text{M}}$ are of the same order of magnitude) and are strongly temperature dependent. At high temperatures ($10^3/T < 3^\circ\text{K}^{-1}$) the exchange is rapid, and a weighted average shift of solvated and bulk HAc is observed. However, instead of decreasing slightly with increasing temperature in the high temperature region as expected from eqn. (2), the shift increases with temperature. This is probably caused by the temperature induced dissociation of the dimers to monomers, resulting in more effective relaxation centers. Using dissociation data from II, and assuming the hyperfine interaction constant to be equal for monomer and dimer ligand protons, we find that about 55 % of the monomer ligands must be HAc at $10^3/T = 3.0^\circ\text{K}^{-1}$ in order to fit the experimental data. The fitted curves in Fig. 3 are calculated from eqns. (6) and (7), resulting in the parameters summarized in Tables 1 and 2. The exchange reaction is assumed to be of the first order. The average

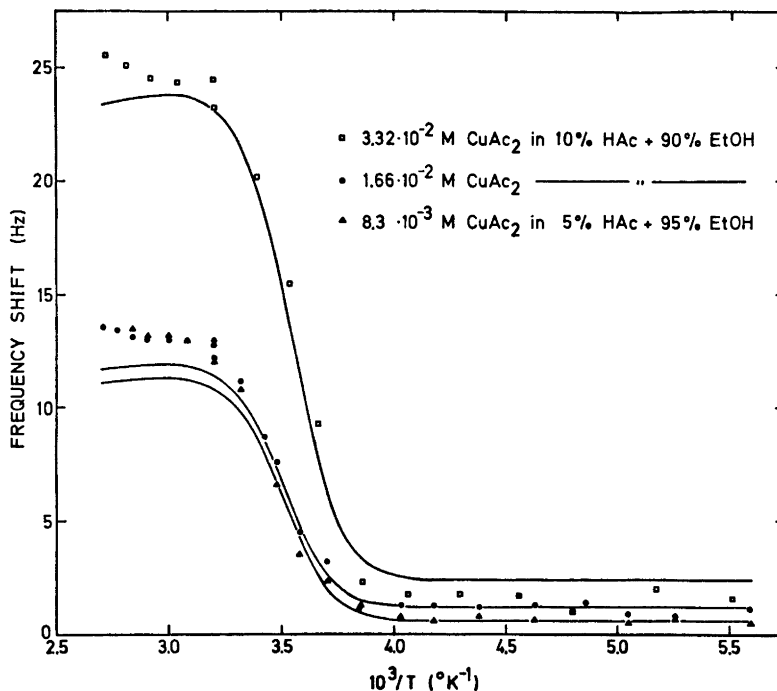


Fig. 3. NMR line shift of HAc methyl protons in ethanol/acetic acid solutions of CuAc_2 , as a function of the reciprocal temperature, copper acetate concentration, and the $c_{\text{HAc}}/c_{\text{CuAc}_2}$ ratio. Points represent measured values. The curves are calculated.

Table 1. Rate constants and activation parameters for HAc axial ligand exchange in ethanol/acetic acid solutions of CuAc_2 at 25°C.

Solvent	c_{CuAc_2} (M)	$1/\tau_M$ (s^{-1})	ΔH (kcal/mol)	ΔS (cal/mol)
EtOH with 5 % HAc	8.3×10^{-3}	2.5×10^4	10.7	-2.7
EtOH with 10 % HAc	16.6×10^{-3}	2.5×10^4	10.7	-2.7
EtOH with 10 % HAc	33.2×10^{-3}	3.0×10^4	10.7	-2.2
EtOH with 10 % HAc H ₂ O content increased to $\sim 0.58 \text{ M}^a$	16.6×10^{-3}	4.0×10^4	10.7	-1.7

^a Primary water content in EtOH and HAc ~ 0.1 and 0.2 M , respectively.

constant low temperature shifts have been added. The frequency shift $\Delta\nu_M$ in Table 2 is nearly constant over the temperature region studied, as expected from eqn. (2), which gives the temperature dependence. The relaxation rate $1/T_{2M}$ follows approximately the temperature function given by the dipolar term in eqn. (1), which means a decrease by a factor of 2.5 when the tempera-

Table 2. NMR line frequency shifts and transverse relaxation rates for HAc ligand protons in ethanol/acetic acid solutions of CuAc_2 .

T (°C)	CH_3 protons				OH protons	
	$\Delta\omega_m/2\pi$ (Hz)		$1/T_{2m}$ (s^{-1})		$1/T_{2m}$ (s^{-1})	
	a	b	a	b	a	b
97	1100		1720			
50	1160		2250			
25	1190	2300	2660	5400	2700	5900
0	1200		3250			
-25	1210		4150			
-50	1190		5600			

a. Values averaged over singlet and triplet states.

b. Values associated with coordination to a triplet state molecule.

ture is raised from -50°C to $+50^\circ\text{C}$. We assume that τ_c is proportional to the ratio of the solvent viscosity to the absolute temperature, η/T , and that its temperature variations is equal to that of the measured PMR line width for pure solvent mixture, shown in Fig. 4. The copper acetate concentration is low and will probably not affect the solvent viscosity to any appreciable amount.

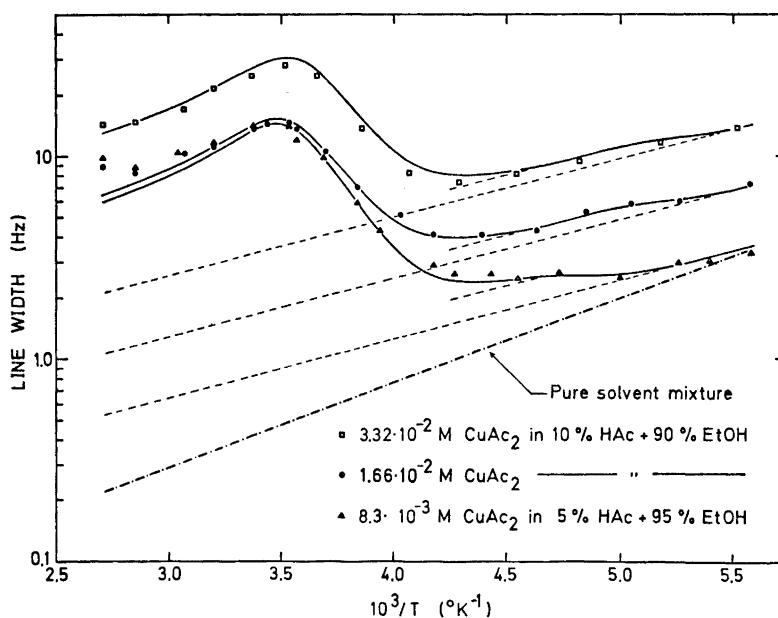


Fig. 4. NMR line width of HAc methyl protons in ethanol/acetic acid solutions of CuAc_2 as a function of the reciprocal temperature, copper acetate concentration, and the $c_{\text{HAc}}/c_{\text{CuAc}_2}$ ratio. Points represent measured values where the solvent contribution (the dash-dot line) has been subtracted. The curves are calculated as explained in the text.

The temperature dependence of the HAc methyl proton signal line width in acetic acid/ethanol solutions of CuAc_2 is shown in Fig. 4. The line width for pure solvent, $1/\pi T_{20}$ has been subtracted, and its contribution is given by the dash-dot line. The straight lines in Fig. 4, extrapolated to higher temperatures by the broken lines, represent the temperature dependence of the contribution of the paramagnetic molecules to the proton relaxation outside the coordination shell, $1/T_{2A}$. Eqn. (4) implies that the slope is given by the slope of $1/T_{20}$, multiplied by the factor $[3 + \exp(\Delta/kT)]^{-1}$, and the magnitude should be proportional to the copper acetate concentration. This is supported by the results.

As the temperature is raised, chemical exchange sets in. Note that a significant step rise in the line width occurs already at $\sim -70^\circ\text{C}$. This step is proportional to the ratio $c_{\text{CuAc}_2}/c_{\text{HAc}}$, and must be assigned to the contribution from a second coordinated HAc ligand. Using the dipolar term in eqn. (1), inserting the values: $\tau_c = 10^{-10}$ s, $x = 0.5$, and $r = 6.3$ Å, the calculated contribution to the line width is consistent with the observed values extrapolated to 25°C , provided the coordination number is equal to one. It is suggested that the second coordinated HAc molecule is hydrogen-bonded to the carboxyl oxygen opposite to the hydrogen bond formed by the axial ligand, as shown in Fig. 5. The distance of closest approach seems reasonable, and a solvation number of one is compatible with steric and space factors. No effect on the shift can be seen, indicating that the unpaired electron spin density is small at the methyl protons position, belonging to the second solvated HAc ligand. An order of magnitude estimation of the chemical exchange rate can be done with the use of eqn. (5), setting $\Delta\omega_M = 0$. Then the step rise should just reach its half maximum for $1/\tau_M = 1/T_{2M}$. This leads to an exchange rate constant $1/\tau_M = 230$ s $^{-1}$ at -67°C ($10^3/T = 4.85^\circ\text{K}^{-1}$) for the second solvated HAc ligand in the driest solution used. But the uncertainty is great, in view of the small effects compared to possible experimental errors.

The chemical exchange of the axial ligands begins to affect the spectrum at $\sim -50^\circ\text{C}$ ($10^3/T = 4.5^\circ\text{K}^{-1}$). The fully drawn curves in Fig. 4 are calculated from eqns. (5) and (7), using the same parameters as in the interpretation of the line shifts. The line width contribution from pure solvent $1/\pi T_{20}$ has been subtracted. The contribution from the second solvated ligand, and from dipolar interaction beyond the coordination shell, represented by the broken

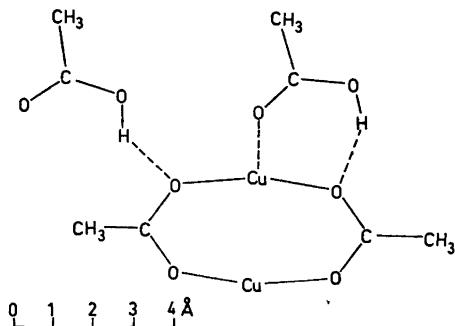


Fig. 5. Assumed structure of a copper acetate dimeric molecule (only two bridges shown) with one axial HAc ligand and one second coordinated HAc ligand.

lines, are included. As stated in the discussion of the line shift, the dissociation of dimers to monomers increases with temperature, and leads to more effective relaxation centers. However, no correction has been applied for this. Hence, the calculated line width and line shift are too small at high temperatures.

The addition of water slightly accelerates the chemical exchange reaction, as demonstrated by the rate constants given in Table 1.

The assumed structure of the copper acetate dimeric molecule with one axial ligand and one second solvated ligand is shown in Fig. 5. Taking approximate dimensions from this model, $r_{\text{CH}_3} = 4 \text{ \AA}$ and $\psi \approx 0^\circ$ for the axial ligand, and using $g_{\parallel} = 2.42$, and $g_{\perp} = 2.08$, similar to values of copper acetate crystal,⁴ the dipolar contribution to the shift is estimated from eqn. (3) to be about 17 % of the observed line shift. Insertion of the remaining effective contact shift into eqn. (2) leads to a hyperfine interaction constant, $A/h = 1.07 \times 10^6 \text{ Hz}$ for the HAc methyl protons on the axial positions of a triplet state dimeric molecule. Applying eqn. (1) and the deduced effective relaxation rate $1/T_{2M} = 2660 \text{ s}^{-1}$ at 25°C , taking $\tau_c = 10^{-10} \text{ s}$ from I, gives an electron spin relaxation time, $\tau_s = 2.6 \times 10^{-10} \text{ s}$. The dipolar and hyperfine interaction contribution to the proton relaxation rate $1/T_{2M}$ are of the same magnitude.

b. Hydroxyl proton signal. For temperatures below $+50^\circ\text{C}$, the hydroxyl proton transfer between acetic acid and ethanol goes fast, compared to ligand exchange, and down to -40°C , only an averaged hydroxyl line from bulk HAc and EtOH can be seen. The proton transfer between the two solvent components is the dominant cause of the temperature behaviour of the observed hydroxyl line width, as shown in Fig. 6.

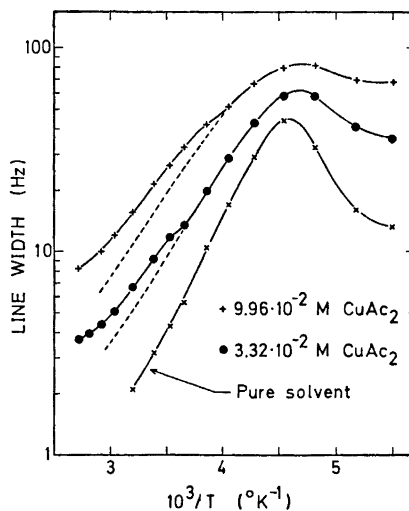


Fig. 6. Observed PMR line width of the OH group in ethanol/acetic acid solutions of CuAc_2 as a function of c_{CuAc_2} , and the reciprocal temperature.

A significant step rise in the line width, proportional to the ratio $c_{\text{CuAc}_2}/(c_{\text{HAc}} + c_{\text{EtOH}})$, occurs at the same temperature as the exchange of the axial ligands sets in. At $9.96 \times 10^{-2} \text{ M CuAc}_2$ in EtOH, with 10 % HAc, the increase in the line width is about 5 Hz. Using eqn. (1), this figure agrees well

with a coordination number equal to one, and a spin-to-closest proton distance 3.4 Å, provided only dipolar interaction is effective. A hyperfine interaction constant, similar to that for methyl protons, should have given a hydroxyl line shift of about 6 Hz in the 9.96×10^{-2} M CuAc_2 solution. But as no significant step in the line shift can be seen, the hyperfine interaction must be smaller. The dipolar shift is nearly zero, because the factor $(3\cos^2\psi - 1) \approx 0$ for the axial ligand hydroxyl protons. The similarity of the temperature behaviour of the OH and CH_3 line widths shows that whole HAc ligand molecules exchange. This result favours the ligand bond mechanism proposed in II, where it is suggested that the axial ligand hydroxyl group may form an additional hydrogen bond to the oxygen of one of the dimer acetate bridges. The contribution of the copper acetate dimers to the hydroxyl proton relaxation beyond the coordination shell is of reasonable size in relation to the molecular geometric dimensions.

As far as we can see, no data exist in the literature concerning the hydroxyl proton transfer between acetic acid and ethanol in solution. Our results for the pure solvent mixture, 10 % HAc in EtOH, were fitted to the modified Bloch equations for chemical exchange between two sites, ignoring broadening due to processes other than exchange. The observed temperature independent chemical shift difference $(\Delta\omega_{\text{HAc}} - \Delta\omega_{\text{EtOH}})_{\text{OH}}/2\pi = 400$ Hz was used. The resulting kinetic parameters are: rate constant $1/\tau_{\text{HAc}} = 6.5 \times 10^4 \text{ s}^{-1}$ at 25°C, and activation energy $\Delta H = 5.0$ kcal/mol.

COMMENTS

We have now found the electron relaxation time $\tau_s = 2.6 \times 10^{-10}$ s for Cu_2Ac_4 with HAc ligands, while in I we deduced $A/h = 4.4 \times 10^5$ Hz and $\tau_s = 11 \times 10^{-10}$ s for Cu_2Ac_4 with EtOH ligands from relaxation and average shifts of CH_2 and CH_3 protons. The treatment of shift data in I, using the averaged shift, is doubtful. The five ethyl protons are coupled together and relax by preference *via* the CH_2 protons, which probably come closest to the unpaired electron spins. Thus the A/h value for the CH_2 protons will determine the main hyperfine interaction contribution to the relaxation rate for the ethyl group. The CH_2 line is shifted 6.3 Hz downfield for 0.166 M solution of CuAc_2 in EtOH, and leads to $A/h = 6.9 \times 10^5$ Hz and $\tau_s = 4.5 \times 10^{-10}$ s, which is closer to our values for Cu_2Ac_4 with HAc ligands. Both in ethanol and acetic acid solution, the ESR line of Cu_2Ac_4 is broad and not observable, due to zero field splitting, so no comparison with the deduced τ_s values can be made.

The A/h and $1/T_{2M}$ value for the HAc ligand CH_3 protons, associated with a triplet state dimeric copper acetate molecule, are of the same order of magnitude as the values reported for MeOH ligand CH_3 protons in methanol solution of Cu^{2+} ions.¹² $A/h = 1.05 \times 10^6$ Hz and $(1/T_{2M})_{52^\circ\text{C}} = 7000 \text{ s}^{-1}$, respectively.

The thermodynamic and kinetic parameters for the chemical exchange reaction of HAc ligands are related to the structure of the activated complex involved in the exchange. The relatively low entropy change, attributed to the axial ligand exchange process, indicates that no extra particle is formed or removed during the transition time. Hence, we suggest that the axial ligand

exchange means that the second coordinated ligand becomes an axial ligand and *vice versa*.

The estimation of the exchange rate parameters will be influenced on whether we take the singlet-triplet relaxation to go slow or fast, compared to the ligand exchange. The latter case is assumed to apply here. The former case leads to an exchange rate constant three times larger than reported here, while ΔH remains unaltered to within the experimental errors.

CONCLUSIONS

The PMR line shift and line width behaviour in acetic acid/ethanol solutions of CuAc_2 confirm that HAc molecules are preferred as axial ligands on dimeric Cu_2Ac_4 molecules.

Comparisons of the OH and acetic acid CH_3 signals support that the axial ligand hydroxyl proton exchanges coincidentally with the corresponding methyl group. This leads to the assumption that the axial ligand hydroxyl group perhaps forms a hydrogen bond to one of the carboxyl oxygens of the dimer acetate bridges.

At low temperature, evidence is seen for a second coordinated HAc ligand, probably hydrogen-bonded to the carboxyl oxygen opposite to the hydrogen bond formed by the axial ligand.

Without knowledge of the spin-lattice relaxation time for the HAc axial ligand protons, the correlation time τ_c and the electron spin relaxation time τ_s cannot be determined independent of each other.

Because of model uncertainties, the derived numerical values may have considerable errors.

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