Multinuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 10.[1] Proton, Carbon-13, and Aluminium-27 Spectra of Aluminium Acetate at Very High Magnetic Field

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Proton, ^{13}C, and ^{27}Al n.m.r. spectra together show that aluminium acetate solutions probably contain two principal species of complex cation in which the aluminium is octahedrally co-ordinated by water, hydroxide, and acetate ligands. Fine structure in the ^{1}H n.m.r. spectra of partially deuteriated species show that each aluminium atom is co-ordinated by three water molecules and that each hydroxide interacts with many more than three water molecules. This and the quantitative data are consistent with the presence of dimeric $(H_2O)_3Al(OH)Al(H_2O)_3$ units with co-ordinated acetate. This may be either bridging or monodentate. Bidentate co-ordination as seen in the solid which precipitates from these solutions is much less likely.

The compound aluminium acetate and its solutions has been known since about 1812. It has been used as a pharmaceutical preparation for the relief of inflammatory conditions, particularly in the German speaking countries, and also latterly in the U.S.A. judging by entries in *Chem. Abstr.* The preparation has also found wide technological application as an agent for dying, printing, and waterproofing.[2] One problem which is mentioned constantly in the older literature is the stability of the solutions and much effort has gone into producing solutions which remain clear for long shelf lives. The solid which precipitates is in fact a basic acetate, $Al(OH)(O_2CMe)_2$, whose composition was only really defined quite recently,[3] though this and similar formulations had been discussed previously.[4-9] As purchased the formulation is often given as a dimer. This compound is not soluble in water and does not melt on heating.

We have previously described our interest in this system as arising because the cation $[Al(H_2O)_6]^{3+}$ is a stronger acid than is acetic acid and so if co-dissolved with sodium acetate the acetate anion is protonated and the aluminium hydrolysed.[10] Solutions containing aluminium salts and sodium acetate are generally of reasonable stability and can be examined at leisure by spectroscopic methods. This contrasts with Hood and Ihde's report which leaves the impression that precipitates are formed rapidly.[3] The pharmaceutical work, however, makes it clear that precipitates generally only appear on standing and we find that heating is needed if precipitation is required. It seems that our laboratory is cooler than that of Hood and Ihde! It also seems clear that the species present in solution is not the same as that which precipitates. The low-field ^{27}Al n.m.r. spectra of these solutions depend upon the ratio $[O_2CMe]/[Al^{3+}]$ which we shall call t. As acetate is added, the intensity of the sharp resonance of Al^{3+} is diminished and a broad unresolved peak appears in its skirts. Above $t = 1.5$, the amount of aluminium detected in the spectrum begins to diminish as a third, broad resonance develops and which is not registered at low magnetic field. The rate at which Al^{3+} was lost as t increased indicated that the overall hydrolysis ratio[1] of the species formed was 2 so that if we were observing pure hydrolysis then these were oligomers of an $[Al(OH)_2]^+$ fragment.[10] We tentatively suggested that if the base-hydrolysed solutions contained a dimer then the acetate solutions should contain $[Al_2(OH)_4]^{2+}$ species. The previous two papers[1,11] have described how new spectroscopic data have led us to modify considerably our view of the nature of the oligomer formed upon base hydrolysis and we will describe here our new findings for the acetate system.

Experimental

In contrast to the detailed chemistry of these solutions, the methods of sample make-up are quite trivial, consisting of co-dissolving aluminium chloride or perchlorate hydrated salts and sodium acetate to a given t value. Variations in t produce virtually no changes in the spectra of the new species formed and, in order to try and introduce a new variable into the work, some samples were made up using either sodium propionate or sodium butyrate. The ^{27}Al and ^{13}C n.m.r. spectra were obtained in aqueous solution using added $[^2H_6]$acetone as lock and standard in the latter case. Samples were also dried and the resulting solids dissolved in either $[^2H_6]$acetone or $[^2H_3]$acetonitrile in order to examine the proton spectra. Partial deuteriation was obtained either by allowing the $[^2H_6]$acetone solutions to stand for sufficient time or by making the initial solution in a H_2O–D_2O mixture. Spectra were run at frequencies of 400 (^{1}H), 100.5 (^{13}C), or 104.2 MHz (^{27}Al) using a Bruker HX400 cryo instrument, and variable-temperature work used the Bruker temperature controller. In general no precipitates were formed in the solutions measured during the time of measurement and if precipitates did form then the data were rejected.

No pH titration experiments were done as previous work had shown that no changes in the ^{27}Al n.m.r. spectra of the new species could be detected other than in the relative concentrations of new species and the monomer Al^{3+}.[10]

Results

Aluminium-27 N.M.R. Data.—Our earlier results seemed to indicate that the acetate solutions and the oligomer in the base-hydrolysed solutions were rather similar. The high-field spectra show however that the broad line at about 4 p.p.m. is much broader in the acetate solutions, and at the same time the hydrolysis ratio of the species formed is smaller, 2.0 rather than 2.5. To attempt to substantiate that the base and acetate systems were different we examined how the linewidths change with temperature. For the base-hydrolysed solutions the oligomer resonance narrows at first with increase in temperature and then broadens again as some exchange process intervenes. The room-temperature linewidth is *ca.* 450 Hz.[11] For the acetate system

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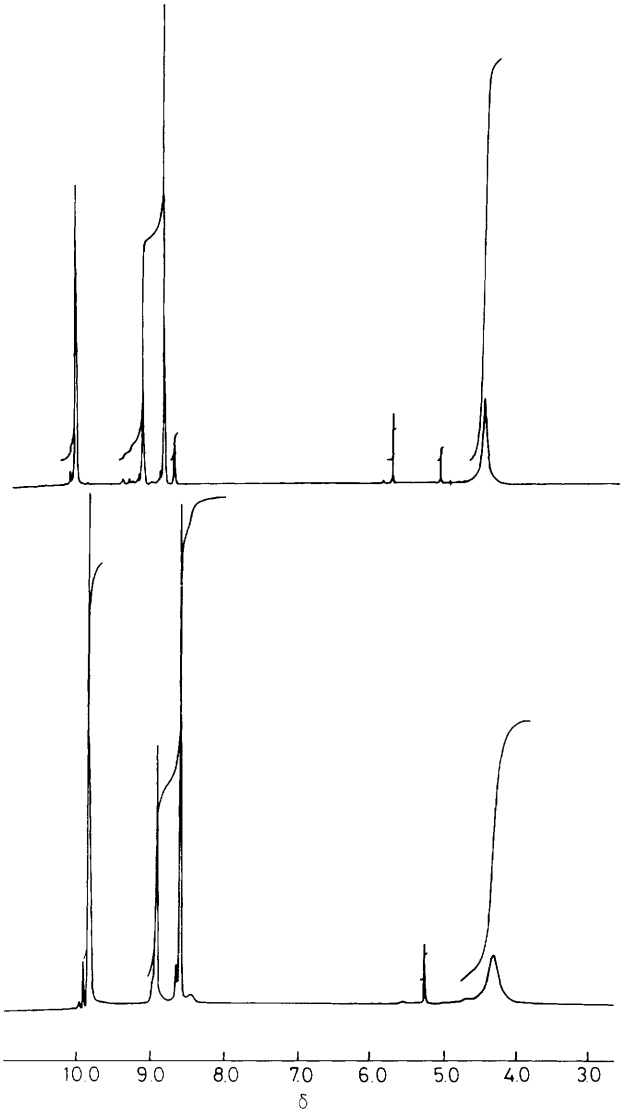


Figure 1. Proton n.m.r. spectra of aluminium propionate solutions prepared as described in the text with $t = 1.0$ and transferred to [$^2H_6$]acetone solution. The upper trace was taken at −30 and the lower at 0 °C. The resonances are due to $[Al(H_2O)_6]^{3+}$ at δ *ca.* 10, bound water at 8—9, bound hydroxide at 4.6—5.6, and free water at *ca.* 4.3. The small spikes just low field of the water lines are due to partially deuteriated hydrates. The spectra of the organic part of the system are omitted. The major components show very little tendency to exchange whereas the minor ones broaden significantly by 0 °C

with $t = 1.5$ and [Al] = 1.0 mol dm^{-3}, the linewidth is 1 000 Hz at 20 °C and falls progressively to 275 Hz at 90 °C. A plot of log(linewidth) against $1/T$ is linear and there is no evidence of exchange. The chemical shift also changes with temperature from *ca.* 4.2 p.p.m. at 25 °C to 2.8 p.p.m. at 90 °C. The two systems therefore behave quite differently and we are observing different species.

In view of the dramatic way in which dilution alters the composition of base-hydrolysed solutions in which oligomer is present, converting this into the tridecamer,[11] it seemed wise to repeat the dilution experiment with an acetate solution. Up to 100-fold dilution was tried and this did not lead to the formation of any tridecamer over a period of days. All that occurred was a narrowing of the broad resonance and a slight reduction in the proportion of visible Al that it represented, though about half the expected aluminium signal intensity was lost in the most dilute solution, and some change in composition has taken place.

*Carbon-*13 *N.M.R. Data.*—These were obtained for aqueous solutions at −10 °C for solutions with $t = 1.5$, 2.5, or 5.0. Two carbonyl and two methyl signals are observed indicating the presence of free and co-ordinated acetate. The carbonyl resonance in particular shows signs of further splitting as t increases so that there are several co-ordination environments. The integrals of the spectra, which are not in any way accurate because of different nuclear Overhauser enhancement (n.O.e.) effects, indicate that perhaps 1—1.5 acetate ligands are complexed per aluminium atom. Thus the species present in solution must contain both hydroxide and acetate ligands and 0.5—1 OH per aluminium also. Warming the solutions to room temperature causes the ^{13}C n.m.r. signals to coalesce so that there is rapid exchange of acetate on the complexes even though the aluminium environment is little affected by this exchange.

Proton N.M.R. Data.—These are shown in Figure 1. The form of the spectra of the complexed species alters very little with t or with replacement of acetate by its higher homologues. Two sharp resonances are observed due to co-ordinated water at δ 9.20—9.25 and 8.90—8.95 and a single hydroxide resonance at 5.8—5.9. There are also a number of minor resonances but these can be ignored since the main resonances are predominant. The spectra remain well resolved even at 0 °C and show much less tendency for proton exchange than the other systems that we have reported. The presence of co-ordinated OH is confirmed and also of a substantial proportion of co-ordinated water which differentiates the species completely from the solid phase which precipitates and which is water free. The integrals for the co-ordinated water cannot be measured accurately because of the presence of the minor species and their intensity ratio varies between 1.21 and 2.00. There is some indication that this ratio varies with t or with the type of anion and while the result is not clear it is evident that there is some variability in the two types of co-ordinated water. The ratio between the total of these and the hydroxide resonance is less variable, though difficult to measure accurately because of the small size of the hydroxide integral. It varies from 13.04 to 14.70, with one value of 17.22, and suggests that a total of seven bound water molecules exist for each bound hydroxide but that the two types of water indicate the presence of two types of complex. The water/hydroxide ratio is high, too high to produce the polymeric type of structure we need, and we have also to take into account the co-ordinated acetate. To give a hydrolysis ratio of 2, the ratio water:OH:acetate has thus to be in the range of 7:1:3 to 7:1:1.

Partial Deuteriation.—This leads to the generation of the isotopic fine structure which we have already described.[1,11—14] The co-ordinated water can be HOH, HOD, or DOD and the first two give proton resonances with a significant isotope shift so that the signal of bound water becomes an unequal doublet whereas that of OH remains a singlet. This is seen in Figure 2. If more than one water molecule is co-ordinated to an aluminium atom then the distribution of deuterium on the others influences the isotope shift of each individual so that the doublets are further split by fine structure whose pattern depends upon the percentage deuteriation and the number of water molecules co-ordinated. Such fine structure is well resolved in Figure 2 on the resonances of both water and OH. There must therefore be more than one water ligand per aluminium atom and we ought to be able to count their number. Figure 3 shows the hydroxide resonance in detail. Such spectra were obtained for several degrees of deuteriation in order to ensure that the correct models had been chosen and three sets of results are given in Figure 4.

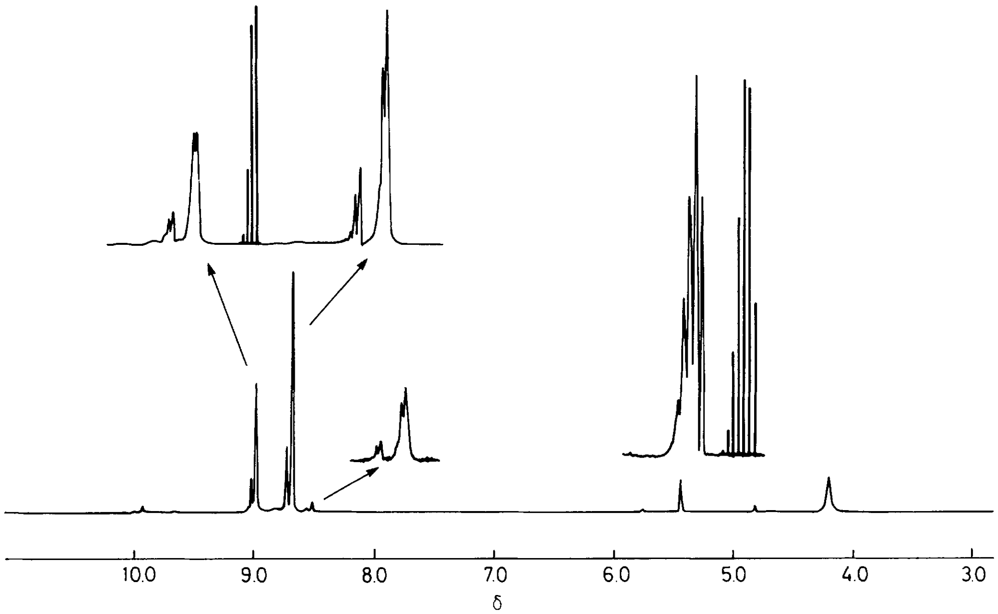


Figure 2. Proton n.m.r. spectra at $-30\,^\circ C$ of aluminium acetate prepared in H_2O–D_2O with $t = 2.0$ and transferred to $[^2H_6]$acetone solution. The resonances of bound water at δ 8.5—9 are now split into doublets due to bound HOH and HOD, the latter to low field. Fine structure can be seen in these resonances and this is displayed in the expanded traces after some line narrowing. The hydroxide resonance, which is not split into an HOH/HOD doublet, also contains fine structure. The stick diagrams are calculated for 19% deuteriation and 4- or 10-site models

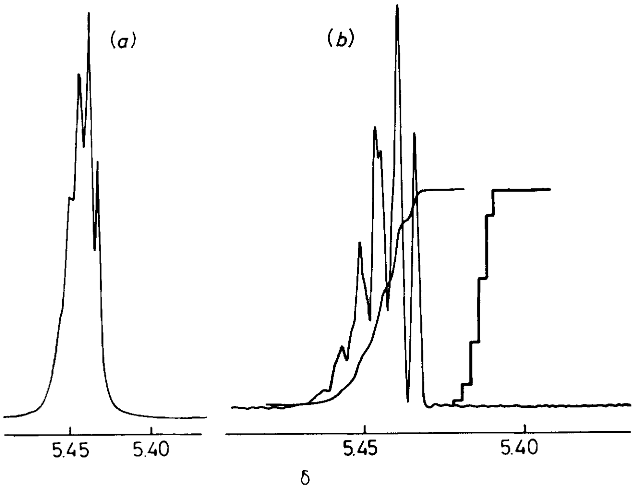


Figure 3. An expansion of the hydroxide trace of Figure 2 with (*b*) and without (*a*) line narrowing and showing the detail of the extra fine structure. The integral trace is compared with a calculated one in the narrowed spectrum since the linewidth progression makes the intensity comparisons inaccurate

It is evident in the spectra that the resonances of HOD, which always appear to low field of those corresponding to HOH, are the better resolved. This is because their relaxation time is not shortened by the HOH dipole interaction. The relaxation behaviour of the hydrated cation $[Al(H_2O)_6]^{3+}$ and its partially deuteriated forms in acetonitrile have been studied in detail,[14] and it has been shown that its rotational correlation time is rather long at 840 ps. This means that its motion is rather too slow for it to remain in the extreme narrowing region in a very-high-field spectrometer and that it is this which causes a lengthening of T_2 (the proton transverse relaxation time) and the observed broadening of the lines. We present no relaxation data in the present paper but note that the appearance of the resonances of the partially deuteriated system is very similar to those of the aqua cation and that the rate of motion of the acetate species must be comparable. On the other hand it is not apparently possible to see fine structure in the oligomer or polymer systems discussed in the previous paper, where the rate of motion is presumably slower.[1] The inference is that in the acetate system we are dealing with small, mobile molecules.

Discussion

Perhaps the most informative data presented here is the fine structure in the proton spectra of the partially deuteriated systems. One can calculate the intensity distribution in the fine structure for a given number of co-ordinated water molecules as follows. If there are n water molecules co-ordinated to a given aluminium atom then any one is influenced by isotopic change on $n - 1$ others, which carry $2(n - 1)$ protons plus deuterons. The principal resonance of either HOH or HOD is thus split into $2(n - 1) + 1$ lines with an intensity distribution given by the terms of the expansion of $(h + d)^{2(n-1)}$, where d is the fractional proportion of sites deuteriated and $h + d = 1$. Different values of n give distinct patterns for a given d and recognition of the value of n is aided by the fact that the exponent $2(n - 1)$ increases in steps of two.[1] To estimate n one proceeds first to estimate d. This is done from the integrals of a major HOH–HOD pair or pairs which gives d to within about ±7%. One then choses, using the apparent multiplicity of the lines, a suitable value for $2(n - 1)$. The fit is not generally exact partly because of the error in calculating d but also because there may be a progressive change in linewidth across a multiplet which distorts the relative line intensities, a particularly strongly perturbed example being the hydroxide resonance in Figure 2. This effect is increased by line narrowing which, while it is useful for counting the multiplicity, exacerbates linewidth differences and introduces the super-Gaussian negative excursions with further intensity distortion. Calculated patterns are thus best compared with relatively poorly resolved fine structure. Proceeding in this way we have been able to show that the fine structure of the water ligands is compatible with a four-site model $[2(n - 1) = 4]$ so

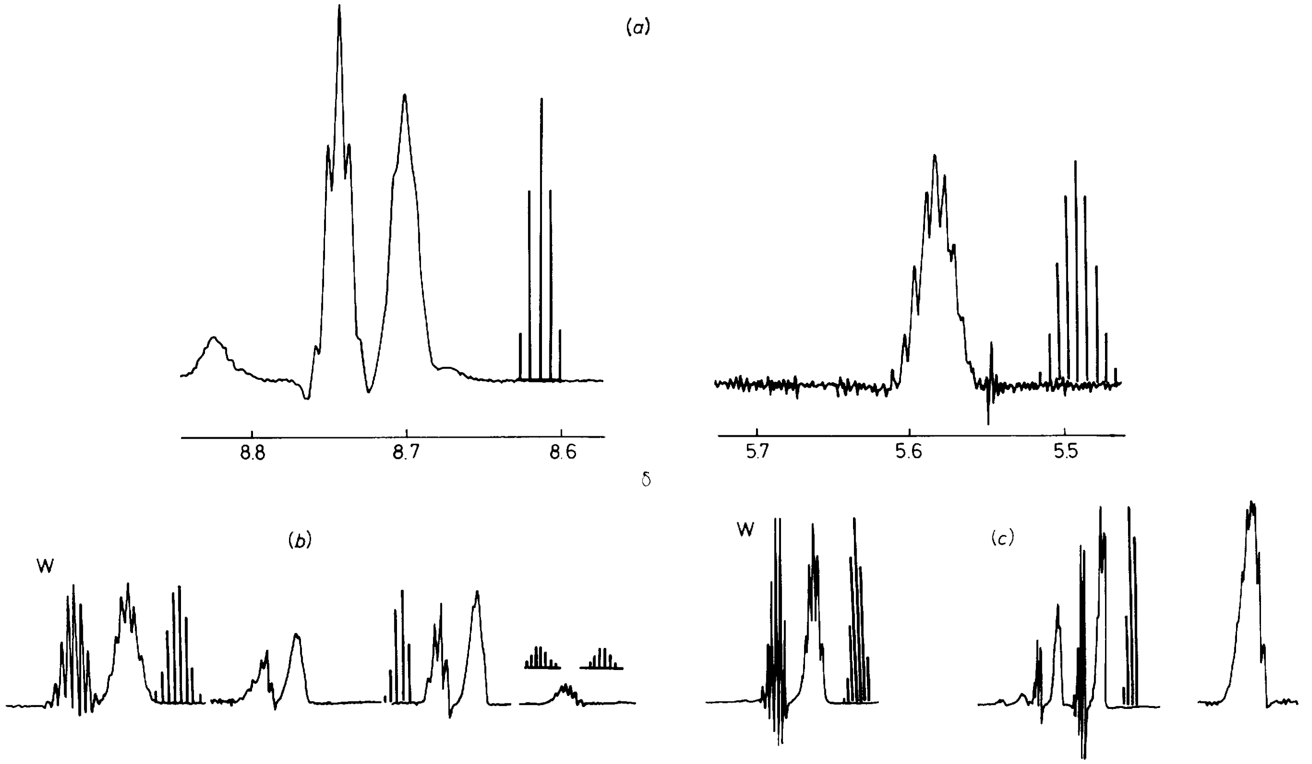


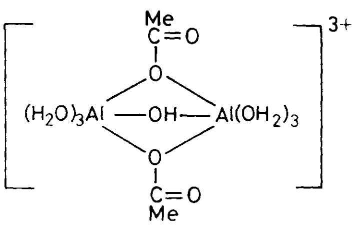
Figure 4. Fine structure observed from different samples with different degrees of deuteriation: (*a*) with acetate to $t = 1.5$ and 50% deuteriation, (*b*) with propionate to $t = 1.0$ and 35% deuteriation, and (*c*) with acetate to $t = 1.0$ and with 23% deuteriation; (*a*) and (*b*) are in [$^2H_6$]acetone and (*c*) in [$^2H_3$]acetonitrile. Spectrum (*a*) shows the resonances for water and OH ligand with stick diagrams calculated for 4- and 12-site models, (*b*) and (*c*) show these resonances together with that of $[Al(H_2O)_6]^{3+}$, W, which provides a check on the calculations; the stick diagrams are thus calculated for 10-, 4-, and 10- and 12-sites (see text)

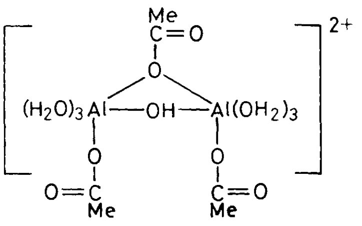
that both sets of resonances come from $Al(H_2O)_3$ moieties.

Isotopic substitution on the ligands also influences the chemical shifts of the hydroxide resonance so that this too has fine structure. It is clear from the various examples illustrated that here the multiplicity is much higher so that a larger number of replaceable protons are involved. This, together with the H_2O/OH ratio of about 7, suggests that each OH is influenced by two $Al(H_2O)_3$ moieties. This implies that the hydroxide fine structure should be that for a 12-site distribution. It comes near to this value but not unequivocally so. The result of Figure 3 fits a 10-site pattern best, though there appear to be two types of OH and this will influence the pattern also. In Figure 4, trace (*a*) is distinctly a 12-site pattern and (*b*), which is of rather low intensity, may be either 10- or 12-site. The hydroxide pattern in trace (*c*), which was obtained in methyl cyanide solution, is different again. Comparison with the pattern for $[Al(H_2O)_6]^{3+}$ shows that the pattern for the OH is split according to either a 12- or 14-site distribution, though neither fits the result correctly. Perhaps again we have overlapping patterns and two types of OH. The fine structure is thus suggestive of the presence of $(H_2O)_3Al(OH)Al(H_2O)_3$ groupings, the fine structure of the bound water being almost unequivocal evidence for this when taken together with the admittedly less clear, though certainly different, hydroxide fine structure.

This conclusion unfortunately poses a problem of logic. If the OH proton is influenced by the water proton isotopic substitution, then the water protons ought to be influenced by substitution on the OH. There would in this case be an odd number of replaceable protons for the group proposed, which is clearly not the case, this being particularly evident for the sample with 50% deuteriation. If, however, there are an even number of OH ligands on each Al, *i.e.* at least two, we cannot obtain anywhere near an H_2O/OH ratio of 7. It follows that we have to assume that the OH does not influence the water ligands, perhaps because its bonding is not influenced significantly by the isotopic substitution. This seems a little strange but is in accord with other observations both with hydrolysed beryllium species,[13] and with the fact that the single water ligand molecule on each of the outer Al atoms of the tridecamer cation shows no fine structure due to the four OH bridges linked to each Al.[1,15]

The proton fine structure thus supports the presence in the species formed of a basic OH-bridged dimeric unit. We have then to introduce acetate ligands in order to complete the structure, and these could be mono- or bi-dentate or bridging. A bidentate ligand seems the least likely, at least for the major species, since this uses up all the valency sites of Al, gives a low total hydrolysis ratio [defining this as $(OH + O_2CMe)/Al$], and leaves a possibly rather labile single OH bridge to hold together a dimer which is not labile to exchange. We suggest three structures as possible for the two major species, based on bridging and monodentate acetate ligands, and favour the doubly bridged species. Exchange of acetate ligands *via* the monodentate ligand should be facile. Variation in the relative amounts of the two species should influence the ^{27}Al n.m.r. chemical shift and account for the small variation observed without necessarily meaning that the dimers should easily dissociate into aluminium monomers. It also seems reasonable for such structures to lose water ligands and bind bidentate acetate on the way to forming the insoluble solid phase, which may well form chain polymers rather than dimers and so explain the lack of solubility.[16] Logically, the water ligands have to be all *cis* since we have had to propose that they will have different chemical shifts if *cis* or *trans* in the oligomer.[1]





$$[(MeOCO)_2(H_2O)_3Al-OH-Al(OH_2)_3(OCOMe)_2]^+$$

The minor components are also of interest because where fine structure is observed in their resonances it always appears similar to that in the main species, albeit difficult to measure at such low intensities. They seem, however, to have much lower H_2O/OH ratios and this indicates somewhat different structures. The minor species represented by the two lines at about 8.7 and 4.8 p.p.m. for instance have a H_2O/OH ratio near unity and one is forced to conclude that we may have the surprising structure $Al(OH)_3(H_2O)_3$.

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