Aluminium-27 and Hydrogen-1 Nuclear Magnetic Resonance Studies of Solutions of Aluminium Salts in Alcohol–Chloroform Mixtures

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The nature of the ionic species formed when $AlCl_3$ or $Al(ClO_4)_3$ is dissolved in various anhydrous alcohols and diluted with $CDCl_3$ has been investigated using ^{27}Al n.m.r. spectroscopy. The alcohols MeOH, PrOH, BuOH, and Bu^iOH show similar behaviour, although the resonances in the higher alcohols are much broader than in MeOH. Ethanol is anomalous, but if this alcohol is diluted with $CDCl_3$ its behaviour becomes normal. The resonances in the diluted alcohols become generally less broad with increasing dilution, and at the highest dilutions evidence is obtained for the presence of the hexasolvate, with a weak, narrow resonance. Addition of water to $AlCl_3$–EtOH solutions produces mixed solvates as already observed for methanol solutions. However, the aluminium resonances are too broad in EtOH to allow adequate analysis of the system and it was found necessary to use low-temperature ^1H n.m.r. spectroscopy. All the mixed solvates could be recognised, although the chemical shift progression of the HOH and EtOH protons across the series of complexes formed was somewhat irregular.

It has recently been shown that aluminium-27 n.m.r. spectroscopy at very high field and frequency (104.2 MHz) can provide much detail about the species present in methanolic solutions of aluminium chloride or perchlorate and can be used to monitor the effect of addition of small quantities of water. In pure methanol, this work showed that the principal species present is $[AlCl_2(MeOH)_4]^+$ together with smaller amounts of $AlCl_3(MeOH)_3$ and possibly $[Al(MeOH)_6]^{3+}$.[1] One feature of the results which was difficult to understand was the fact that the resonance of the hexasolvate was broad (*ca.* 150 Hz) whereas such a symmetrical molecule usually gives rise to a narrow line. It was suggested that this could be due to an exchange between the hexasolvate and a monochloro-cation, which indeed was never visible in any of the spectra. The present work was undertaken in an attempt to solve this problem and to extend our knowledge to the higher alcohols, ethanol, propanol, and butanol, and some of their isomeric forms.

Experimental

Anhydrous alcohols were prepared by the Grignard method.[2] Solutions were made up by weight in a dry-box from anhydrous $AlCl_3$ and the perchlorate solutions were made up from these by double decomposition with a solution of $AgClO_4$. N.m.r. grade deuteriochloroform was added to provide a field–frequency lock; 10% (v/v) was added to the 'pure' alcohol solutions and the effect of increasing chloroform additions was studied in detail, up to 90% (v/v), since it was found that this led to appreciable line narrowing, especially with the higher alcohols. The solution make-up was monitored using aluminium-27 n.m.r. spectroscopy at 23.45 MHz on a Bruker HFX90 instrument since this quickly showed whether the solutions were anhydrous or not, but all the informative spectra were obtained at 104.2 MHz on a Bruker 400 MHz instrument. Ethanol–water solutions were examined in addition using low-temperature ^1H n.m.r. spectroscopy at 400 MHz since the aluminium-27 lines were too broad to resolve the many resonances of the species present in this mixed solvent. Standardisation of the ^{27}Al spectra was carried out by calibrating the spectrometer with $Al_2(SO_4)_3$ in water–$[^2H_2]$water and then adding 1.60 p.p.m. to the results obtained with the $CDCl_3$ lock.[3] The methyl resonance of EtOH was used to standardise the ^1H spectra.

Results

Aluminium Chloride in Several Alcohols with added $CDCl_3$.—The results are summarised in Table 1. If we focus attention on the resonance which appears in all the solutions at *ca.* 9.6 p.p.m., and is in all cases the most intense one, we see that in the 90% alcoholic solutions the linewidth increases rapidly as we move from MeOH to the higher alcohols, from 26 to over 330 Hz. The other resonances broaden also and the highest-field one in effect disappears. In all alcohols but EtOH, the lines narrow if more $CDCl_3$ is added, and the resolution of the resonances is improved to the extent that the high-field resonance is detectable. The features observed are similar to those already reported for MeOH[1] but the breadth of the lines means that we cannot expect to extract much information for the higher alcohols. Similar species are formed, although the hexasolvate is not much in evidence. However, the ethanolic solution seems to be anomalous. The shifts are out of sequence and the lowest-field line appears at 11.13 p.p.m., close to a very weak feature in the spectra of the methanol solutions. The shifts become more normal as the solution is diluted but the main resonance at 8—9 p.p.m. actually broadens. At the highest dilution a sharp, weak line appears at 2.85 p.p.m. which may be due to the hexasolvate. These changes are not understood, but they cannot be due to water contamination, which as will be shown produces different effects. The branched-chain alcohols Pr^iOH and Bu^iOH did not give useful results. Aluminium chloride is only slightly soluble and the lines are very broad, *cf.* the last line in Table 1. The spectra are shown in Figure 1.

Methanolic Solutions of $AlCl_3$ *and* $Al(ClO_4)_3$ *with added* $CDCl_3$.—The narrow high-field line seen in the above solutions suggested that dilution with $CDCl_3$ might enable us to observe the hexasolvate in methanolic solutions where the resonances are at their narrowest. Dilutions of 90, 30, and 10% (v/v) MeOH were used and the aluminium salt concentration was kept low so that the alcohol was always present in excess of 6 mol per mol Al. The results are in Table 2 and the spectra are shown in Figure 2. Dilution leads to the appearance of a narrow high-field line in the $AlCl_3$ solutions, but not in the perchlorate solutions where the line ascribed to hexasolvate is always broad, although another feature appears at 7 p.p.m. The chemical shifts of the resonances vary across the dilution series. It is not known whether this is a real feature of the aluminium

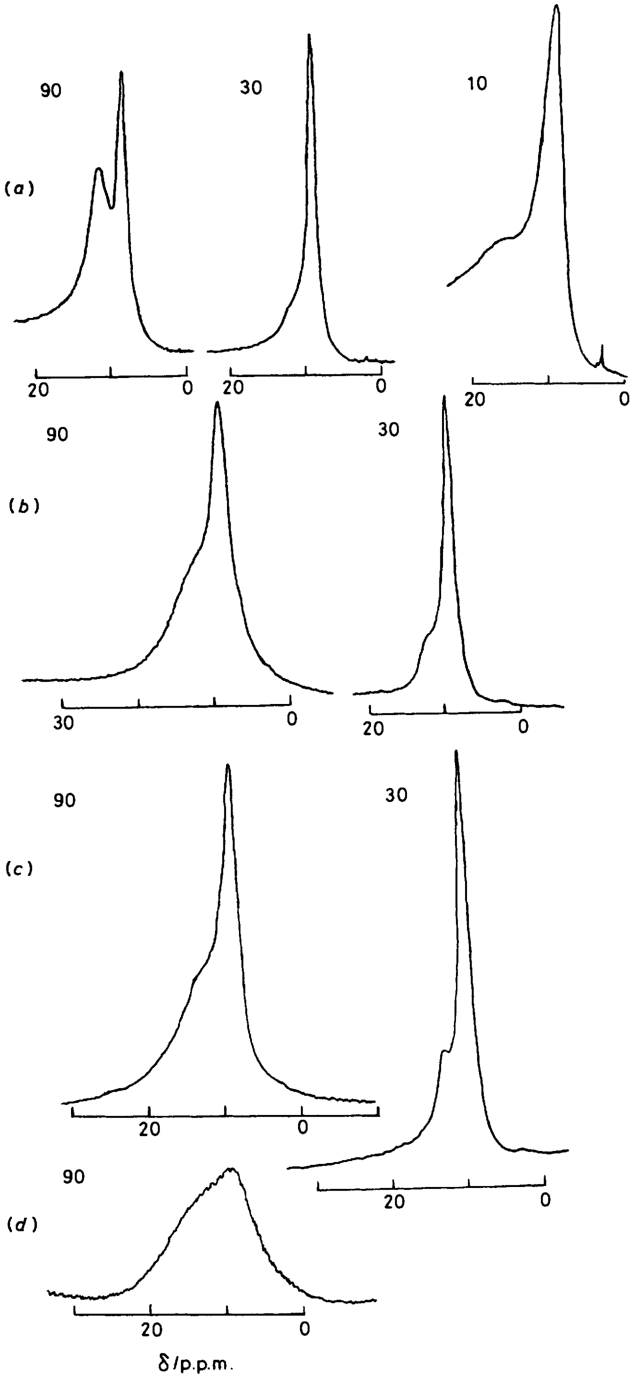

Figure 1. Aluminium-27 n.m.r. spectra at 104.2 MHz of $AlCl_3$ in anhydrous alcohols diluted with $CDCl_3$. All spectra are on the same horizontal scale. The alcohols are EtOH (*a*), Pr^{n}OH (*b*), Bu^{n}OH (*c*), and Bu^{i}OH (*d*). The figures on the spectra are the % (v/v) of the alcohol. Note the weak lines near 3 p.p.m. at 10 (*a*) and 30%, v/v (*a*—*c*)

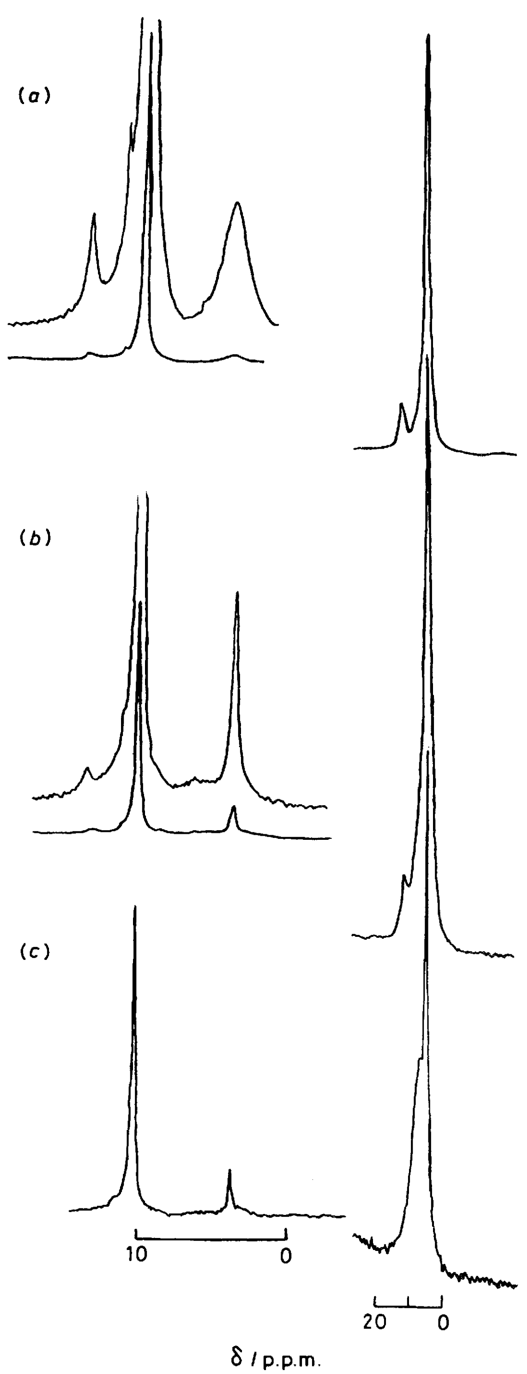

Figure 2. Aluminium-27 n.m.r. spectra at 104.2 MHz of $AlCl_3$ (on the left) or $Al(ClO_4)_3$ (on the right) dissolved in MeOH with added $CDCl_3$ to 10 (*a*), 30 (*b*), or 90%, v/v (*c*). The horizontal scales are not the same, the right-hand one being 4.5 times more compressed than the left-hand one. Two traces at different gains are shown for the two left-hand spectra in (*a*) and (*b*)

chemistry or is due to solvent effects on the $CDCl_3$ lock. Certainly, there are hydrogen-bond interactions between the two solvent components.[4]

Ethanolic Solutions of $AlCl_3$ *and* $Al(ClO_4)_3$ *with added* $CDCl_3$.—The results for $AlCl_3$ are in Table 1 and for the perchlorate in Table 3, while the spectra are illustrated in Figure 3. The $AlCl_3$ spectra are unique in that the two main components in 90% EtOH are close together and of comparable intensity. The high-field one is in roughly the same position as a weak feature seen in many spectra in MeOH at 11.1 p.p.m. both here and previously.[1] Diluting the solution causes chemical shifts and changes which give the spectrum a more regular appearance, and the narrow, high-field line appears. The resonances, with this exception, are always broad. Conversion into perchlorate solutions produces poorly resolved spectra which have features of those seen in MeOH. The lines are best resolved in the most dilute solution, although both are shifted upfield for either chemical reasons or because of solvent effects

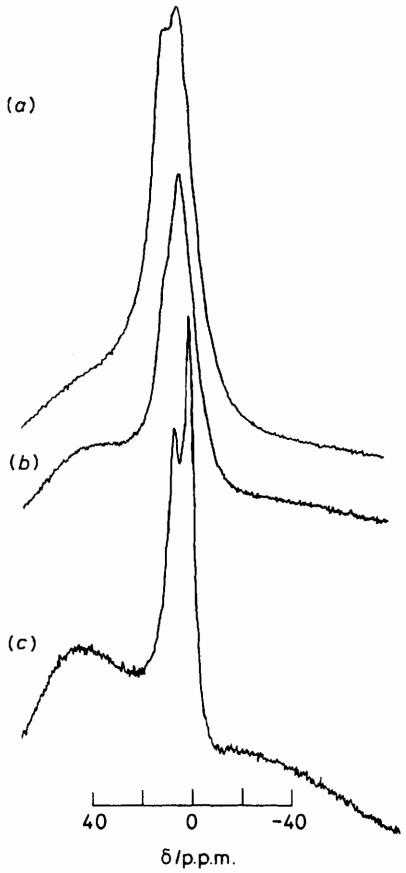

Figure 3. Aluminium-27 n.m.r. spectra at 104.2 MHz of $Al(ClO_4)_3$ in anhydrous EtOH with added $CDCl_3$ to 10 (*a*), 30 (*b*), or 90%, v/v (*c*). The broad underlying resonance which is particularly evident in (*c*) (the one most dilute in Al) is due to alumina solid in the probe

on the lock. In no case in perchlorate solutions is a very sharp resonance seen at high dilution which can be ascribed to the hexasolvate.

Mixed Ethanol–Water Solutions of $AlCl_3$ *with* 50% (v/v) $CDCl_3$.—These were examined initially using n.m.r. spectroscopy but the resonances were so much broader than those obtained in the methanol–water system that no useful information could be extracted, although the form of the spectra is clearly similar to those obtained in the latter solvent,[1] Figure 4. Deuteriochloroform was added in an attempt to obtain better resolution, but it transpired that in the aqueous solutions the chloroform concentration was limited to 50% since above this the aqua-aluminium chloride salt precipitated out. The form of the ^{27}Al spectra was essentially unchanged although the resolution was in fact slightly worse than for the 10% solutions. It has already been shown that ^{1}H n.m.r. spectroscopy can distinguish several types of bound OH proton in ethanolic solutions of $AlCl_3$ contaminated with small quantities of water, even at low magnetic field strengths,[5] and we decided to examine our solutions at 400 MHz to try and distinguish the many mixed species present. The $CDCl_3$ was expected to reduce the rate of proton exchange and so the 50% solutions were used for these studies and complex, well resolved spectra were obtained at −10° C, Figure 5.

Discussion

It will be immediately obvious from Figure 1 that the usefulness of ^{27}Al spectroscopy is much reduced for the higher alcohols.

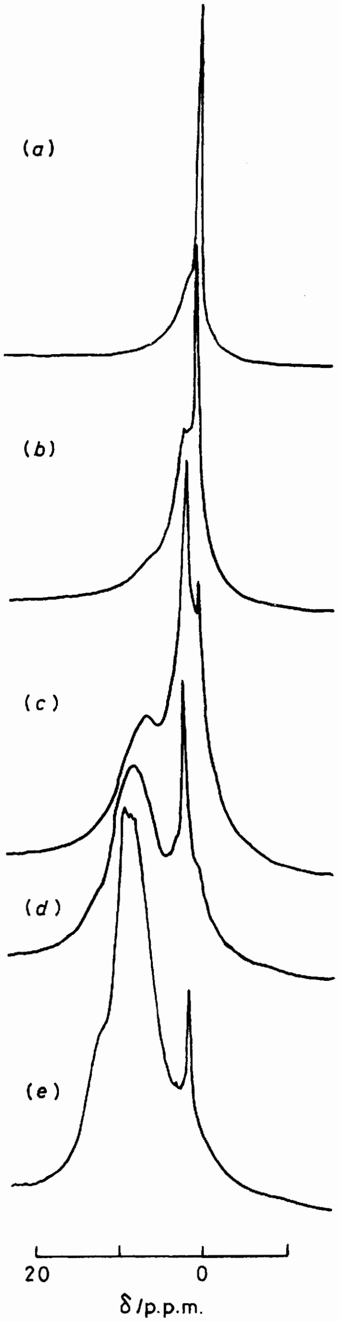

Figure 4. Aluminium-27 n.m.r. spectra at 104.2 MHz of $AlCl_3$ in EtOH–$CDCl_3$ (50:50, v/v) with added water to give $[H_2O]/[Al]$ of 5.3 (*a*), 4.3 (*b*), 3.2 (*c*), 2.1 (*d*), and 1.1 (*e*). The spectrum of the anhydrous solution is in Figure 1 [(*a*) 30 is the nearest in composition]

Nevertheless, with the exception of ethanol, the behaviour of the n-alcohols is comparable and we can accept that a chloro-complex is formed in all cases, even in ethanol if diluted with $CDCl_3$. The unique behaviour of this pure alcohol cannot at present be explained, although as shown below it could probably be resolved using ^{1}H n.m.r. spectroscopy. The line narrowing seen at high dilution is probably due to reduced hydrogen bonding between the complexes and bulk alcohol,[4] and to a change in the exchange processes present, the latter particularly allowing the detection of a narrow resonance which can be assigned to the hexasolvate.

The spectra of the aluminium salts dissolved in methanol also

Table 1. Aluminium-27 n.m.r. parameters of solutions of $AlCl_3$ in anhydrous alcohols with $CDCl_3$ diluent to 100%

Alcohol	% (v/v)	[Al]/mol dm^{-3}	Chemical shifts (δ/p.p.m.) and linewidths (*W*/Hz) in parentheses[a]					
MeOH	90	0.32	13.05 (52)	10.7 (w)	9.62 (26)	3.71 (187)		
EtOH	90	0.50		11.13 (260)	8.01 (130)			
	30	0.51	12.1 (sh)		8.80 (117)			2.35 (w)
	10	0.48	*ca.* 16 (br)		9.6 (365)		2.85 (*ca.* 13, n)	
Pr^{n}OH	90	0.49	13.1 (br sh)		8.55 (364)			
	30	0.17	12.1 (sh)		9.1 (157)			2.35 (vw, nn)
Bu^{n}OH	90	sat.[b]	13.6 (br sh)		9.2 (335)			
	30	sat.[b]	12.6 (*ca.* 200)		9.6 (154)			2.4 (vw, nn)
Bu^{t}OH	90	sat.[b]	*ca.* 14.4[c]		9.6[c]			

[a] w = weak, sh = shoulder, br = broad, v = very, n = narrow, and nn = not narrow. [b] Implies less than 0.2 mol dm^{-3}. [c] Combined width of these two resonances 1 085 Hz.

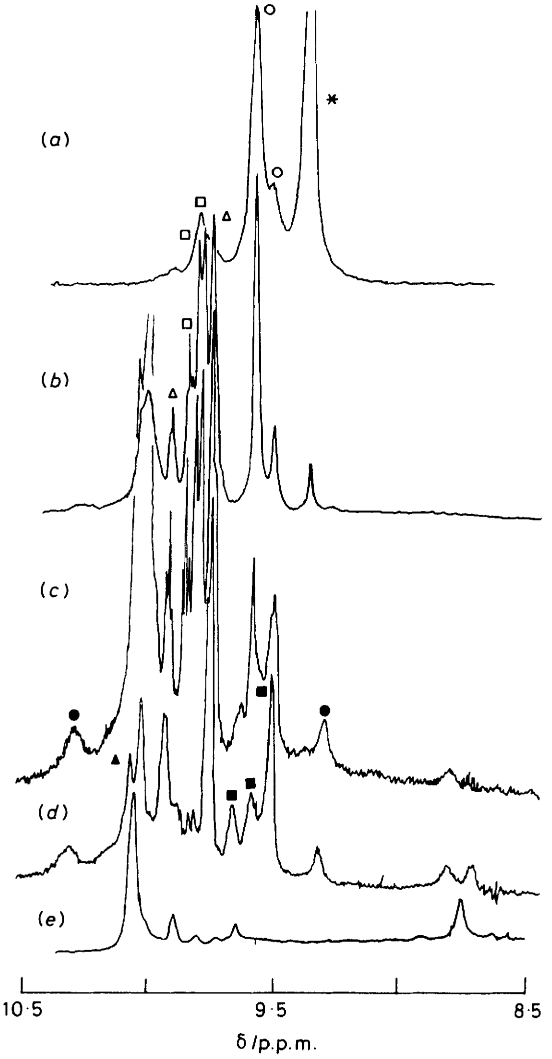

Figure 5. Proton n.m.r. spectra at 400 MHz of the OH proton region of EtOH–$CDCl_3$ solutions of $AlCl_3$ with added water to give $[H_2O]/[Al]$ of 5.3 (*a*), 3.2 (*b*), 2.1 (*c*), 1.1 (*d*), and 0 (*e*). The spectra were obtained at *ca.* −10° C. The lines are coded to correspond to Table 4

show this feature. With $AlCl_3$, the broad line at *ca.* 3 p.p.m. becomes much narrower as $CDCl_3$ is added and with 90% $CDCl_3$ attains 26 Hz with a weak, underlying, broad resonance which is probably due to $[AlCl(MeOH)_5]^{2+}$. This species must then be the predominant one of the two in the pure alcohol, and exchange between this and the hexasolvate is likely since the narrow line would show up on top of the broad one down to very low concentrations of the hexasolvate. The chemical shift progression is then rather surprising: trichloro < dichloro < monochloro > hexasolvate. Marked changes also occur with the perchlorate salt as its solutions are diluted with $CDCl_3$. The small line due to the remnant dichloro-complex is removed upon dilution and a broad component appears at 7 p.p.m. overlapping the broad line at 3 p.p.m., assigned previously to hexasolvate.[1] The relative intensities make it unlikely that this new resonance is due to remnant monochloro-complex, and its shift is a little low field of that assigned to this resonance of the chloride solutions. It seems therefore that we are forced to assume that it is due to a perchlorate complex, and further, that the high-field line is due to the hexasolvate but broadened by interaction with the anion. Such an assignment is of course somewhat uncertain but is supported by the fact that perchlorate complexes of aluminium have been detected in methyl cyanide.[6]

The perchlorate salt in ethanol gives rather broad resonances (Figure 3) of uncertain position but the general behaviour seems similar to that observed in methanol.

Mixed Complexes.—The ^{27}Al n.m.r. spectra in Figure 4 change with water addition in very much the same way as observed previously for methanolic solutions.[1] The progressive loss of the chloro-complex and the formation of mixed water–ethanol complexes is clear. The species *fac*-$[Al(EtOH)_3(H_2O)_3]^{3+}$ and $[Al(H_2O)_6]^{3+}$ show up clearly as narrow resonances, the reason for the long relaxation time of the former now being well understood.[1,7,8] Unfortunately, the resonances are otherwise far too broad even to attempt meaningfully to extract quantitative data and we must turn to the ^1H n.m.r. spectra of Figure 5 for information on the behaviour of the individual complexes. The proton spectra contain at least 15 resonances which increase and/or decrease in intensity as the solution composition changes. Two are triplets and so can be assigned to EtOH hydroxy-protons. Other groups of lines change intensity in a parallel manner and so can be attributed to the same complex, and this, coupled with the fact that a complex with a given number of water molecules tends to have its maximum concentration when the quotient $[H_2O]/[Al]$ is equal to that number,[1,9] allows the resonances to be assigned with a reasonable degree of certainty without making any assumptions as to the chemical shifts of the protons in each species. The assignments and chemical shifts are given in Table 4 and the resonances in Figure 5 are coded appropriately. We summarise the reasoning we have used to make these assignments as follows: the anhydrous solution has two principal

Table 2. Aluminium-27 n.m.r. parameters of solutions of $AlCl_3$ or $Al(ClO_4)_3$ in anhydrous MeOH with $CDCl_3$ diluent

	MeOH (%, v/v)	[Al]/mol dm^{-3}	Chemical shifts (δ/p.p.m.) and linewidths (*W*/Hz) in parentheses						
(*a*) $AlCl_3$									
	90	0.32	13.05 (52)	10.7 (w)	9.62 (26)		3.7 (187)		
	30	0.11	13.2 (*ca.* 60)	11.2 (w)	10.2 (31)	*ca.* 6 (br, w)	3.7 (42)		
	10	0.037			10.45 (32)		4.0 (26)		3.0(vw)
(*b*) $Al(ClO_4)_3$									
	90	0.18			10.2 (150)			3.2 (175)	
	30	0.061			11.2 (140)	7.3 (w, br)		4.2 (200)	
	10	0.02				*ca.* 7 (sh)		4.2 (150)	

Table 3. Aluminium-27 n.m.r. parameters for solutions of $Al(ClO_4)_3$ in anhydrous EtOH with $CDCl_3$ diluent[a]

EtOH (%, v/v)	[Al]/mol dm^{-3}	Chemical shifts (δ/p.p.m.) and linewidths (*W*/Hz) in parentheses	
90	0.49	9.7[b]	3.2[b]
30	0.16	*ca.* 9.7[c]	2.2[c]
10	0.054	6.0 (*ca.* 350)[d]	0.2 (*ca.* 550)[d]

[a] Results for $AlCl_3$ solutions in Table 1. [b] Combined width 1 800 Hz, lines overlap. [c] Combined width 1 400 Hz, lines overlap. [d] Lines resolved.

resonances which must be $AlCl_2E_4$ and $AlCl_3E_3$ (E = EtOH, W = H_2O, charge omitted for brevity). That the former is a singlet suggests that the chloride ligands are *trans*, not *cis* as has been proposed previously,[1] and this is more in accord with the narrow resonance seen for this line in MeOH.[1,8] At the same time we will note that *cis*/*trans* isomerism is not evident in these spectra. These two resonances are lost as water is added and some hydrated chloro-forms appear briefly: AlW_2E_4 appears early and gives a 1:1 doublet, although with a remarkably large chemical shift between the two components of 1.0 p.p.m., AlW_3E_3 gives a 1:2 doublet with the weaker component showing coupling to CH_2. There are presumably both the *fac* and *mer* isomers present, the latter in excess,[1] although only one can be identified with confidence. The species *cis*-AlW_4E_2 gives a 2:2:1 triplet, the weaker component being a 1:2:1 triplet due to CH_2 coupling. Again, the *trans* isomer (a 1:4 doublet) was not detected. Somewhat surprisingly, the two species $AlWE_5$ and AlW_5E seem to give rise to groups of lines in the same part of the spectrum and which overlap at the intermediate water compositions. The expected 2:1:4 pattern of the former and the 10:1 pattern of the latter are reasonably reproduced in the observed spectra. The species AlW_6 is easily identified and is some 0.2 p.p.m. to high field of its position in aqueous solution.[10]

The chemical shifts of the various protons in this family of complexes seem to follow no obvious pattern. They are clearly not influenced strongly by the relative numbers of the two components (W,E) complexed to the metal, or even by the presence of two chloride anions. We suspect that the shift may be influenced by the way the alkyl groups of the ethanol shield the first-sphere hydroxyl protons from the solvent and the chloride anions which no doubt are present to some extent in the second co-ordination sphere. Clearly data are required for different salt solutions in ethanol and in methanol, in order to separate the various influences. Such an approach should allow us to understand the complex interrelation of electric field and second-sphere polarisation in such systems.

Table 4. Proton chemical shifts (t = triplet) and assignments to mixed solvates in aqueous ethanol solutions of $AlCl_3$

Solvate	δ/p.p.m.	Assignment	Code in Figure 5
AlW_6	9.44		✱
AlW_5E	9.64	W, 10 H	○
	9.56	E, 1 H	
AlW_4E_2	9.83	W, 4 H	□
cis form with	9.85	W, 4 H	
two types of W	9.89 (t)	E, 2 H	
AlW_3E_3	9.78	W, 6 H	△
	9.95 (t)	E, 3 H	
AlW_2E_4	10.33	equal nos.	●
trans?	9.35	W and E protons	
$AlWE_5$	9.69	W, 2 H	■
	9.62	E, 1 H (*trans* to W)	
	9.56	E, 8 H	
$AlCl_2E_4$	10.06		▲
$AlCl_2WE_3$ (?)	10.10	W?	
$AlCl_3E_3$ (?)	8.75		
$AlCl_3WE_2$ (?)	8.84		

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