Multinuclear (^1H, ^{27}Al, and ^{35}Cl) Nuclear Magnetic Resonance Studies of Solutions of Aluminium Salts in Methanol, Aqueous Methanol, and Aqueous Acetone

J. W. Akitt,* Robert H. Duncan, and Christine Setchell
The School of Chemistry, The University of Leeds, Leeds LS2 9JT

The nature of the ionic species formed when $AlCl_3$ or $Al(ClO_4)_3$ is dissolved in anhydrous methanol has been investigated using ^1H, ^{27}Al, and ^{35}Cl n.m.r. spectroscopy. The principal species in $AlCl_3$ solution is $[AlCl_2(MeOH)_4]^+$, although surprisingly, the monochloro-complex does not appear to form. Solutions of $Al(ClO_4)_3$ contain the hexasolvate which exhibits a remarkably broad ^{27}Al line, presumed to be due to interaction between the anion and the hexasolvated cation. Addition of water to $AlCl_3$ solutions results in the formation of mono- and di-aquadichloro-complexes although these are quickly and progressively replaced by chloride-free complexes with mixed methanol–water solvation spheres. The results indicate that most of the methanol is displaced from the cations when six water molecules per aluminium cation have been added. No tetrahedral aluminium species were detected.

Solutions of aluminium salts in alcohols have been much studied using n.m.r. techniques. An early ^{27}Al investigation indicated that the aluminium was octahedrally co-ordinated when $AlCl_3$ was dissolved in ethanol [1,2] and low-temperature proton spectroscopy gave a solvation number of six for $Al(ClO_4)_3$ in methanol.[3] Grasdalen,[4,5] however, found a solvation number of four for $AlCl_3$ in both ethanol and n-propanol, and noted that the bound hydroxyl resonance had fine structure so that several hydroxyl environments existed. The presence of bridged polymers was postulated in order to reconcile these findings with the ^{27}Al results. Martin and Stockton [6,7] extended this work and used ^1H and ^{13}C n.m.r. to examine solutions of $AlCl_3$, $Al(ClO_4)_3$, or their mixtures in ethanol and found that the solvation number depends on the anion. Richardson and Alger [8] obtained comparable results although they found that the solvation number could vary over a range, and that for $Al(ClO_4)_3$ in methanol it could be less than six. It thus appears that the anions are bound to the aluminium in the first co-ordination sphere, but that this remains octahedral. The problem has recently been taken up by Russian workers who have repeated the ^{27}Al work.[9–11] They find a single narrow resonance 10 p.p.m. to low field of $[Al(H_2O)_6]^{3+}$ and interpret their results as octahedral solvation with ion pairing in the second co-ordination sphere.

Clearly these observations are not consistent and further evidence is required to draw correct conclusions. If an aluminium cation were solvated by six alcohol molecules then, in principle, one would expect to observe a narrow line close to the position of $Al^{3+}(aq)$. We therefore need to know if such a resonance exists in a solution with a solvation number of six, and whether this coincides with the line at 10 p.p.m. seen in $AlCl_3$ solutions. We report here some very-high-field ^{27}Al n.m.r. spectra obtained in an effort to resolve this question together with supporting evidence from ^1H and ^{35}Cl n.m.r. spectroscopy.

Experimental

Anhydrous methanol containing about 5% of CD_3OD as lock was prepared by the Grignard method.[12] N.m.r. grade deuterioacetone was used as received. Solutions were prepared from anhydrous $AlCl_3$ and the perchlorate solutions were made from these by double decomposition with a solution of anhydrous $AgClO_4$. Manipulations were carried out in a glove-bag and samples in n.m.r. tubes were stored in a closed container over silica gel for transport to the high-field spectrometer.

Proton, ^{27}Al, and ^{35}Cl n.m.r. spectra were obtained initially on a Bruker HFX3 at frequencies of 90, 22.6, and 6.49 MHz respectively, the last two using unlocked field. Later spectra were obtained for ^1H and ^{27}Al on a Bruker 400-MHz instrument where the aluminium frequency is 104.2 MHz and a locked mode of operation is standard. The Fourier-transform mode of data collection was used throughout. Standardisation was obtained by setting up the spectrometer using CD_3OD in 1 mol dm^{-3} aqueous $Al_2(SO_4)_3$ solution and the $[Al(H_2O)_6]^{3+}$ signal was assigned 0.0 p.p.m. It was established that all the aluminium present contributed to the observed signals, *i.e.* there were no unobservedly broad lines, by comparing spectral intensities with those of an aqueous solution of known concentration.

It appeared initially that the system should lend itself to dehydration using 2,2-dimethoxypropane, reaction (1).[8,13] The

$$H_2O + Me_2C(OMe)_2 \xrightarrow{H^+} 2MeOH + Me_2CO \quad (1)$$

appearance of acetone in the proton spectra of solutions so treated indicated that reaction had proceeded but the resulting 'anhydrous' solution had an unusual ^{27}Al spectrum, due it transpired to the fact that acetone and possibly the dimethoxypropane also interact with Al^{3+} in methanol. This led us to make a brief investigation of the system $AlCl_3$–acetone. Such solutions are unstable and quickly develop a brown colouration due presumably to dehydration of the acetone and its polymerisation. They are thus never simple systems.

In addition the solvation number for $Al(ClO_4)_3$ in ethanol was obtained and is quoted below, and some ^{35}Cl measurements were also made on this system.

Results

Proton Spectra.—At 400 MHz and 25 °C, $AlCl_3$ in MeOH shows a single OH resonance and three principal methyl resonances, the bulk signal at an assumed 3.38 p.p.m. and two small ones due to bound molecules at 3.72 and 3.65 p.p.m. with intensities in the ratio of *ca.* 1 : 2. Two very small resonances of bound molecules were also discernible at 3.7 and 3.63 p.p.m. These signals persisted at −20 °C and the OH resonance split into two components with the bound OH at 10.96 p.p.m. As implied in earlier work,[8] the latter resonance is a singlet, although there is a small, poorly resolved shoulder to high field. These results indicate that the OH-proton and whole-molecule exchange occur at different rates. An $Al(ClO_4)_3$ solution at 25 °C showed bound-methyl resonances at 3.71,

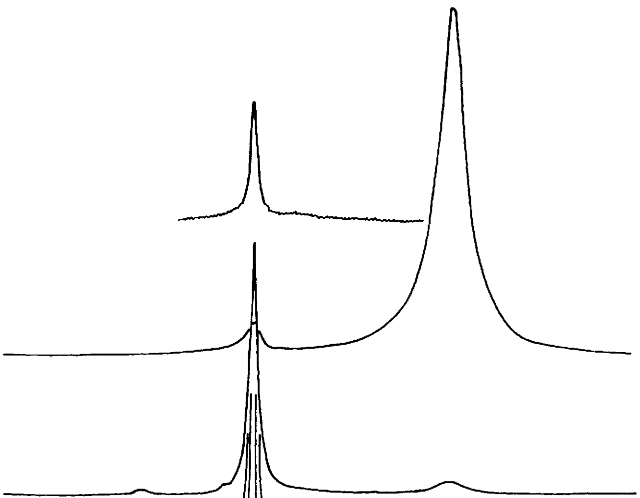

Figure 1. Aluminium-27 spectra of aluminium salts dissolved in anhydrous methanol. The lower four curves are of $AlCl_3$ at concentrations of 0.05 (lowest), 0.1, 0.25, and 0.5 mol dm^{-3}, spectrometer frequency 104.2 MHz. The uppermost, short trace is of 0.75 mol dm^{-3} $AlCl_3$ at 22.6 MHz; the weak, broad, high-field component can just be discerned. The remaining upper, full trace is from 0.5 mol dm^{-3} $Al(ClO_4)_3$ at 104.2 MHz. The vertical scales of the spectra are all different, although the horizontal scales are the same (in Hz)

Table 1. Aluminium-27 n.m.r. parameters of solutions of $AlCl_3$ or $Al(ClO_4)_3$ in anhydrous methanol

Solute	Concn. (mol dm^{-3})	Chemical shift/ p.p.m.[a]	Linewidth/ Hz	% Al
$AlCl_3$	0.75 [b]	12.98	122	7.7
		9.0	35	76.5
		0.78 [c]	177	15.8
	0.5 [d]	13.15	62	3.0
		9.62	31	82.6
		3.45	109	14.4
	0.25 [d]	13.17	57	3.0
		9.57	26	80.7
		3.52	161	14.8
	0.1 [d]	13.15	52	2.8
		9.55	23	83.6
		3.33	234	12.2
	0.05 [d]	13.16	48	2.8
		9.55	23	85.3
		3.2	244	10.8
		e	—	0.9
$Al(ClO_4)_3$	0.75 [b]	6.2 [c]	134	10.3
		0.78 [c]	182	89.7
	0.25 [d]	9.35	57	5.0
		3.15	104	95.0
	0.5 [d]	9.96	136	6.0
		3.04	243	94.0
	0.25 [d,f]	10.01	79	0.7
		3.09	198	99.3

[a] Aqueous $Al_2(SO_4)_3$ as reference with common CD_3OH lock. The resonance near 13 p.p.m. is due to $AlCl_3(MeOH)_3$, that near 10 p.p.m. to $[AlCl_2(MeOH)_4]^+$, and that near 3 p.p.m. to the hexasolvate. [b] 22.63-MHz spectra, unlocked field. [c] This result is clearly inaccurate, presumably due to field drift in the unlocked mode. [d] 104.2-MHz spectra, CD_3OH lock. [e] Peak associated with remnant water in this most dilute of the solutions. [f] With $AgClO_4$ in excess.

3.69, and 3.65 p.p.m. in the intensity ratio of *ca.* 1 : 2 : 2; the peak at 3.63 p.p.m. remained small and of doubtful significance. The solvation numbers (from integrals of bound and free OH or CH_3 groups) obtained in this (in parentheses) and in earlier work are summarised below, including figures for ethanolic solution for comparison:

	Solute	
Solvent	$AlCl_3$	$Al(ClO_4)_3$
MeOH	3.7,[8] (4.5 ± 0.6)	6,[3] 6.0 [8]
EtOH	4,[4,7] 4.0 [8]	(6.2 ± 0.6)

Aluminium-27 Spectra.—The 22.63-MHz spectra of $AlCl_3$ solutions showed a single resonance at about 9 p.p.m., as found by the Russian workers,[9-11] although curve analysis [14,15] suggested that two weak resonances might be present, one to low and one to high field. Unfortunately, such a spectrum hardly provides the substantive evidence required to solve the problem posed here, as reference to Figure 1 will show. Aluminium perchlorate solutions gave a broader line to high field, possibly coinciding with the high-field component in the $AlCl_3$ spectrum.

The 104.2-MHz spectra, however, are of a quality to resolve all doubts. Three resonances are present in the $AlCl_3$ solutions and only small changes in the spectra occur as the aluminium concentration is reduced from 0.5 to 0.05 mol dm^{-3}. Aluminium perchlorate solutions give a principal resonance close to, but not coinciding with, the high-field resonance in $AlCl_3$ solutions. A small resonance remained near 9 p.p.m. This may indicate that all the chloride ions have not been precipitated with the silver perchlorate. Certainly, adding an excess of $AgClO_4$ reduces further the intensity of this line, a fact which suggests that removal of chloride may not be as quantitative as has been assumed in such systems, The spectra are illustrated in Figure 1 and the spectral parameters are given in Table 1.

In order to check whether remnant water was affecting our results, we also obtained spectra on a series of $AlCl_3$ solutions to which measured quantities of water had been added. The results are shown in Figure 2 and the parameters are in Table 2. Comparison of Figures 1 and 2 makes it clear that the influence of water is detectable only in the most dilute anhydrous solutions, and amounts to a water content of less than 0.73 mol per mol Al at 0.05 mol dm^{-3}. The actual level is perhaps about half this and the methanol must then be about 0.017 mol dm^{-3} in water or less.

A spectrum of $AlCl_3$ dissolved in $[^2H_6]$acetone obtained from a freshly opened vial of n.m.r. solvent is shown in Figure 4.

Chlorine-35 Spectra.—The two anions Cl^- and ClO_4^- give narrow resonances in aqueous solution, the infinite-dilution values being 8 [16,17] and 1.2 Hz [16] respectively. If either anion is complexed by a cation then the rate of quadrupolar relaxation is increased because the electric field gradient at the

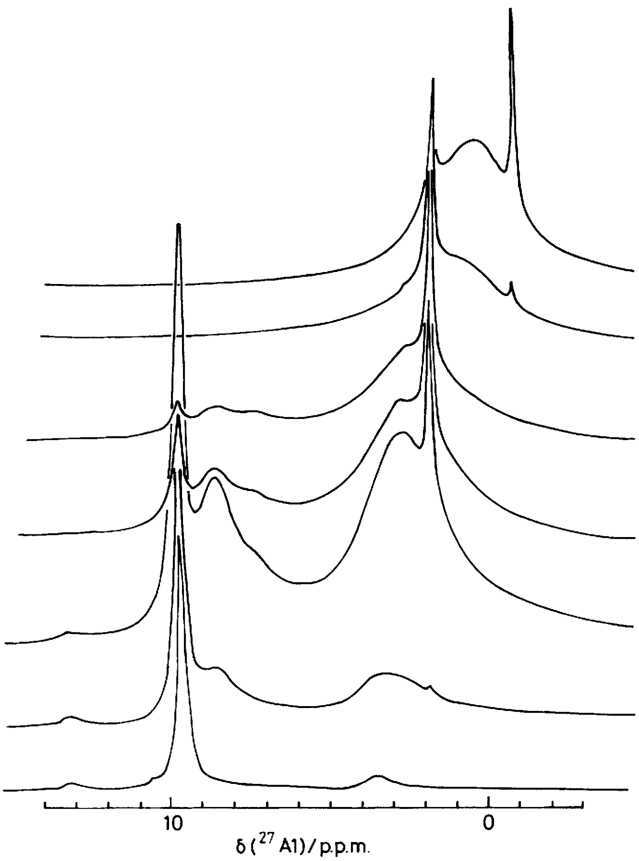

Figure 2. Aluminium-27 spectra of 0.5 mol dm^{-3} $AlCl_3$, in anhydrous methanol and with added water to give various H_2O : Al ratios. The water content increases on going from the bottom to the top of the figure. The vertical scales are not the same. Note the minor components at 10.5, 2.7, 2.5, and 2.3 p.p.m. which appear at different water contents. These have not been included in the tables. The H_2O : Al ratios are 0, 0.73, 1.33, 1.83, 2.44, 3.08, and 4.28.

chlorine nucleus is increased and the rate of motion around the ions is decreased.[18] Studies of linewidth changes in solutions have been much used to follow the complexation of Cl^-,[19,20] for which the effects are large. Smaller changes occur in solutions containing perchlorate but useful information can be extracted.[21,22] In the present studies it was not found possible to detect the ^{35}Cl resonance in alcoholic solutions of $AlCl_3$. Instead, it was necessary to make up a solution of LiCl and add small amounts of $AlCl_3$. The linewidth is 420 Hz in 2 mol dm^{-3} LiCl in MeOH, perhaps due to a charge-transfer interaction with the solvent. Adding a small amount of $AlCl_3$ to give an Al : Cl ratio of 0.077 : 1 increased the linewidth to 1 550 Hz. Clearly, the chloride interacts with the aluminium cation in this solvent. We are not however clear whether this is simply *via* rapid chloride exchange in the otherwise long-lived chloro-complex, or due to a less well defined interaction with the first co-ordination sphere of a hexasolvated complex. Such a question could be resolved by quantitative ^{35}Cl n.m.r., which was not feasible in the original low-field experiments.

The chlorine nucleus in the perchlorate anion is more isolated from its surroundings than is that in the chloride anion and linewidth changes on complex formation are less dramatic. For solutions 2.5 mol dm^{-3} in perchlorate, the linewidth increased from 30 Hz in $LiClO_4$ to 50 Hz in $Al(ClO_4)_3$. Some interaction may be occurring although unknown changes in viscosity could be responsible for the linewidth changes in this case. Support for the existence of an interaction may be obtained from the ^{35}Cl results obtained with ethanolic solutions, where the linewidths obtained for the equivalent pair of samples were 42 and 725 Hz respectively.

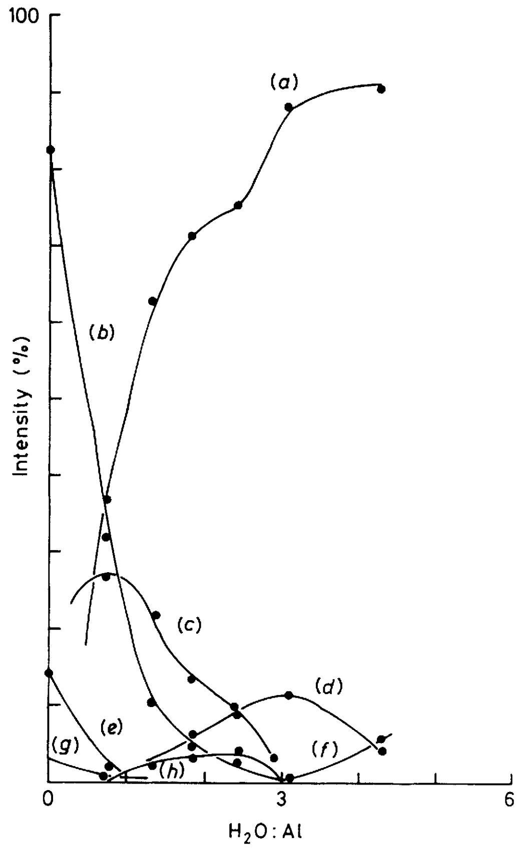

Figure 3. Variation in intensity of the spectral components of Figure 2 as a function of water content. Species: (*a*) mixed H_2O/MeOH solvates; (*b*) $[AlCl_2(MeOH)_4]^+$; (*c*) $[AlCl_2(H_2O)(MeOH)_3]^+$; (*d*) *fac*-$[Al(H_2O)_3(MeOH)_3]^{3+}$; (*e*) $[Al(MeOH)_6]^{3+}$; (*f*) $[Al(H_2O)_6]^{3+}$; (*g*) $AlCl_3(MeOH)_3$; (*h*) $[AlCl_2(H_2O)_2(MeOH)_2]^+$

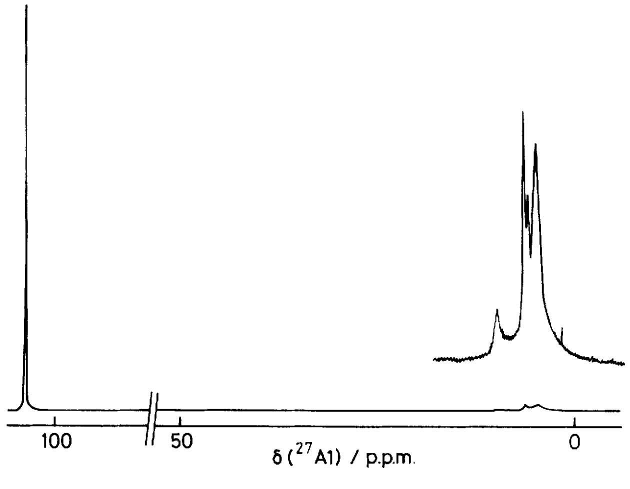

Figure 4. Aluminium-27 spectrum of $AlCl_3$ dissolved in $(CD_3)_2CO$ about 6 h after being made up. A resonance presumably due to $[Al(H_2O)_6]^{3+}$ is already visible (sharp line to high field)

Table 2. Aluminium-27 n.m.r. parameters of 0.5 mol dm^{-3} solutions of $AlCl_3$ in methanol with small additions of water, the shift (δ/p.p.m.), linewidth (*W*/Hz), and intensity (%) are given for each resonance observed[a]

		Assigned species							
$[H_2O]/[AlCl_3]$		$AlCl_3(MeOH)_3$	$[AlCl_2(MeOH)_4]^+$	$[AlCl_2(H_2O)(MeOH)_3]^+$	$[AlCl_2(H_2O)_2(MeOH)_2]^+$	$[Al(MeOH)_6]^{3+}$	Mixed solvates[b]	*fac*-$[Al(H_2O)_3(MeOH)_3]^{3+}$	$[Al(H_2O)_6]^{3+}$
0	δ	13.15	9.62			3.45			
	W	62	31			109			
	%	3.0	82.6			14.4			
0.73	δ	12.95	9.6	8.37		3.3	2.7[c]	1.75	
	W	50	34	193		104	296	16	
	%	0.8	32.1	27.3		2.5	37.0	0.3	
1.33	δ	13.1	9.7	8.5	7.2		2.5	1.75	
	W	50	36	166	107		336	16	
	%	0.4	10.3	21.7	2.5		62.8	2.3	
1.83	δ	13.1	9.63	8.4	7.0		2.3	1.72	
	W	?	36	186	148		365	17	
	%	*ca.* 0	5.1	13.9	3.6		71.3	6.2	
2.44	δ		9.65	8.4	7.0		2.0	1.80	
	W		36	180	151		380	19	
	%		2.2	9.6	4.0		75.3	9.0	
3.08	δ		detectable but immeasurably small resonances in this region				1.0	1.75	−0.8
	W						382	24	23
	%						88.0	11.3	0.7
4.28	δ						0.4	1.80	−0.8
	W						352	33	14
	%						90.4	4.3	5.3

[a] Probable experimental errors of measurement are ±5% in *W*, ±5% of *W* in chemical shift, and ±10% in the intensity. [b] $[Al(H_2O)(MeOH)_5]^{3+}$ to $[Al(H_2O)_5(MeOH)]^{3+}$, excluding *fac*-$[Al(H_2O)_3(MeOH)_3]^{3+}$. [c] The chemical shift of this resonance is variable; the remainder are essentially constant.

Discussion

Anhydrous Methanol.—The observation of a resonance to high field of the main resonance in the $AlCl_3$ solutions is clear evidence that a species is present which has a similar aluminium environment to $[Al(H_2O)_6]^{3+}$ and which may be assigned to $[Al(MeOH)_6]^{3+}$, at least in the first instance. The major resonance must then be attributed to a first sphere complex. The average solvation number of about four, taken together with the existence of the complex containing *cis*-$[AlCl_2(Pr^iOH)_4]^+$ isolated from an $AlCl_3$–Pr^iOH solution,[23] indicates that the resonance should be attributed to the complex $[AlCl_2(MeOH)_4]^+$. The downfield chemical shift is in accord with this assignment and has been observed for chloro-complexes both in methyl cyanide [24,25] and dimethylformamide [26] solution. The relatively narrow linewidth is in accord with a *cis* geometry.[25] The small, broader resonance to low field is logically assigned to the trihalogeno-complex although this cannot have a *fac* stereochemistry which would exhibit a narrow resonance,[25] and must therefore have the *mer* configuration. Somewhat surprisingly, there is no resonance which can be assigned to a monochloro-complex. This should have a narrower line than the dichloro-species [25] and so should be particularly obvious. We have ascertained that all the aluminium present contributes to the observed spectrum, and must therefore conclude that the monochloro-complex is absent.

Replacing the major part of the chloride by perchlorate gives a spectrum which shows principally the high-field line which then must logically be due to hexasolvate. There is however a small but real chemical shift difference between the corresponding lines in the two salt solutions and this suggests the existence of more than one component. The resonance is also far too broad for a typical hexasolvate and the existence of three bound-proton resonances in solutions of both chloride and perchlorate salts indicates that matters may be rather more complicated than the obvious straightforward interpretation. Distortion of the symmetry around the Al is possibly due to steric interaction of the alkyl groups, although one then has to ask why this does not appear to affect the dichloro-complex. Alternatively, the anions may be involved with the first coordination sphere, as occurs with alkylammonium cations.[27,28] It is possible to calculate an average solvation number for $AlCl_3$ solutions from the ^{27}Al spectra based on the above assignments and at 0.5 mol dm^{-3} one obtains 4.26, satisfactorily close to the values obtained by ^1H n.m.r.

The sensitivity of the ^{27}Al spectra to water contamination should be noted. It will thus obviously be insufficient to use ' dry ' reagents as received since even small amounts of water solvate the cation preferentially, perhaps to a much greater extent than would have been expected. This factor may have affected some earlier kinetic investigations in ethanol.[4]

Addition of Water.—Quite small additions of water produce profound changes in the ^{27}Al spectra (Figure 2). The line at 13 p.p.m. is lost quite quickly and those near 9 and 3 p.p.m. develop extra multiplicity, the former also being lost if sufficient water is added. The sequence of events is consistent with progressive aquation both of the dichloro-complex, accompanied by loss of chloride, and of the hexamethanol solvate. The n.m.r. parameters are assembled in Table 2 and the way the concentrations of the various species change as water is added is shown in Figure 3. Two fairly broad resonances appear just to high field of the dichloro-peak, one at 8.4 p.p.m. which reaches its maximum intensity when about one molecule of water has been added per aluminium cation and one near 7.1 p.p.m. which reaches its maximum later, when nearly two molecules have been added. It has been shown that, to a first approximation, where the added component solvates the cation much more strongly than does the solvent, then the point at which a given species attains a maximum concentration is a guide to the number of added component molecules that it contains. The present system is clearly more complex than that contemplated by Covington and Covington,[29] and involves species with and without complexed chloride. The lack of measurable quantities of the monochloro-complex however allows us to assume that the two types of complex exist to some extent independently and so conclude that the two resonances arise from $[AlCl_2(H_2O)(MeOH)_3]^+$ and $[AlCl_2(H_2O)_2(MeOH)_2]^+$ respectively. The effects on the chemical shift of the successive water molecules are similar at 1.25 p.p.m. (first) and 1.34 p.p.m. (second). Very little of the chloro-complexes remain after three molecules of water have been added.

The behaviour in the hexasolvate region is somewhat unusual. Much of the spectral intensity is transferred into this region by the early water additions but only four resonances are observed. Two of these are particularly narrow and so are very obvious. One at 1.75 p.p.m. is at maximum when about three water molecules have been added and must then be due to the *fac* isomer of $[Al(H_2O)_3(MeOH)_3]^{3+}$.[25] This is useful further proof that such a narrow line does indeed arise from such stereochemistry. The narrowness of the line also indicates that exchange between the hexasolvates must be slow. We can see the loss of the line at 3.3 p.p.m.; thereafter the major broad component in this region moves upfield, broadens then narrows and can always be fitted well by a single Lorenzian line. There are admittedly seven different mixed solvates which should appear progressively as water is added, with chemical shifts between 3.3 and −0.8 p.p.m. $\{[Al(H_2O)_6]^{3+}\}$ and with linewidths comparable to the chemical shift difference. The moving resonance is thus a compound line made up of many components of varying intensity. That it remains Lorenzian, without asymmetry, presumably reflects the regular way in which the concentrations of the species vary as water is added.[29] We also note the relatively small proportion of *fac*-$[Al(H_2O)_3(MeOH)_3]^{3+}$ which is formed. This is a more sterically crowded complex than is the *mer* isomer and so appears to be less stable. The chemical shifts of the three resonances ascribed to $[Al(MeOH)_6]^{3+}$, *fac*-$[Al(H_2O)_3(MeOH)_3]^{3+}$, and $[Al(H_2O)_6]^{3+}$ can be rationalised on the basis of a pairwise interaction scheme [30] with the larger ligand giving the larger pairwise effect, and this is further evidence that the line at 3.3 p.p.m. is indeed due to the hexamethanol solvate. Its breadth, especially when compared with the two narrow, higher field lines, remains a puzzle, and we have to assume that interaction between the anion and the alkyl groups is suppressed by the stage that three water molecules have been taken up by the cation.

Anhydrous Acetone: Chemical Dehydration.—The weaker donor-solvent acetone gives a spectrum similar to that obtained in methyl cyanide,[24,25] where the chloride ion is less well displaced from the aluminium and the major component present is $[AlCl_4]^-$. Several octahedral species are also present, and a narrow resonance at 0.7 p.p.m. can be ascribed to $[Al(H_2O)_6]^{3+}$, indicating that the solvent decomposes quite rapidly. 2,2-Dimethoxypropane thus cannot be a satisfactory dehydrating agent in this system, since one of its products reacts to give water and the reagent itself may interact with the cations. The method has been used once previously in related work [8] to dehydrate $Al(NO_3)_3$ and $Al(ClO_4)_3$ hydrate salt solutions and it is now clear that, unfortunately, it should not be used for aluminium salt solutions. This is a great pity since the method is very convenient and easy to use.

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