A Quantitative Study of the Aluminium Trichloride–Acetonitrile System using *X*-Ray Crystallography, Electrical Conductivity, Aluminium-27 and Chlorine-35 Nuclear Magnetic Resonance and Raman Spectroscopy. The Characterization of the Pentakis(acetonitrile)chloroaluminium(III) Ion in the Solid State and in Solution †

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The compounds MCl_3 (M = Al, Ga, or In) yield electrically conducting solutions in acetonitrile. Boron trichloride gives non-conducting solutions and, contrary to previous work, this is interpreted as due to the presence of a molecular solute $BCl_3\cdot MeCN$. The electrical-conductivity data for $AlCl_3$ in acetonitrile are discussed in detail and it is shown that from the results obtained it is not possible to differentiate between 1 : 1 and 1 : 2 electrolyte behaviour. Quantitative Raman and ^{27}Al n.m.r. spectra demonstrate that *ca.* 70% of the aluminium in solutions of $AlCl_3$ in acetonitrile is present in the form of $[AlCl_4]^-$. An *X*-ray single-crystal study of the solid adduct $AlCl_3\cdot 2MeCN$ crystallizing from such a solution shows that this adduct is correctly formulated as the auto-complex $[AlCl(NCMe)_5]^{2+}2[AlCl_4]^-\cdot MeCN$. Further ^{27}Al n.m.r. studies on solutions of $Al[ClO_4]_3$ in acetonitrile and of the solute $AlCl[ClO_4]_2$, in conjunction with the work on $AlCl_3$ demonstrate that $[AlCl(NCMe)_5]^{2+}$ is the major cationic constituent of aluminium trichloride solutions in acetonitrile. The electrical-conductivity, Raman, and n.m.r. data on these solutions are all satisfactorily interpreted by the principal ionization scheme $[AlCl(NCMe)_5]^{2+}2[AlCl_4]^-$ which is the formulation found for the crystal. The ionization of $AlCl_3$, but the non-ionization of BCl_3, in solution in acetonitrile is attributed principally to the ability of aluminium to adopt a co-ordination number of greater than four in ions such as $[AlCl(NCMe)_5]^{2+}$.

ACETONITRILE is widely used as a solvent. It possesses both ionizing and co-ordinating properties, has a relatively low reactivity towards inorganic compounds, and is a poor conductor of electricity.[1] It is not an easy solvent to purify and there is considerable confusion in the literature on studies of solutions in acetonitrile due to the presence of impurities, notably water.[2] For example, electrical-conductivity measurements are frequently carried out at a concentration of 0.001 mol dm^{-3}, corresponding to *ca.* 20 p.p.m. for water as a solute.

A survey of the behaviour of the chlorides of the non-transition elements as solutes in acetonitrile shows that those of Groups 1 and 2 are rather insoluble. However, the adducts $BeCl_2\cdot 2MeCN$ [3] and $MgCl_2\cdot 2MeCN$ [4] have been characterized. The compounds $AsCl_3$,[5] BCl_3,[5] $SeCl_4$,[6] $TeCl_4$,[2] and $SbCl_5$ [2] behave essentially as non-electrolytes. Further, the compounds $BCl_3\cdot MeCN$,[7] $SnCl_4\cdot 2MeCN$,[8] $SbCl_5\cdot MeCN$,[9] and $BeCl_2\cdot 2MeCN$ [10] have all been shown to be molecular by *X*-ray single-crystal structure analysis (with a *cis*-octahedral configuration for the tin compound). There is no substantiated evidence for adduct formation by $SiCl_4$,[11] $GeCl_4$,[11] $AsCl_3$,[5] $SeCl_4$,[6] or $TeCl_4$.[2] A recent study of phosphorus pentachloride solutions in acetonitrile using Raman spectroscopy with laser excitation [12] led to a proposal for two competing equilibria with (2) predominant at

$$2PCl_5 \rightleftharpoons [PCl_4]^+ + [PCl_6]^- \qquad (1)$$

$$PCl_5 \rightleftharpoons [PCl_4]^+ + Cl^- \qquad (2)$$

lower concentrations. Complex formation between acetonitrile and either molecular PCl_5 or the $[PCl_4]^+$ ion [13-15] has not been observed.

The situation with regard to the trichlorides of B, Al, Ga, and In is not well understood. In presenting our results we shall follow a chronological order for a period which covers more than a decade.

RESULTS

Figure 1 summarizes our experimental data on the molar conductivity of acetonitrile solutions of these trichlorides.

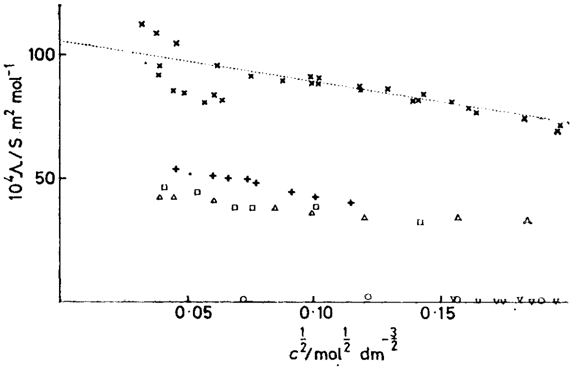

FIGURE 1 The molar conductivity of boron, aluminium, gallium, and indium trichlorides in acetonitrile: (○) BCl_3 (this work); (▽) BCl_3 (ref. 5); (×) $AlCl_3$ (this work); (△) $GaCl_3$ (this work); (+) $GaCl_3$ (ref. 16); (□) $InCl_3$ (this work)

The agreement with earlier work by Schmulbach and Ahmed on boron trichloride [5] and gallium trichloride [16] is acceptable. In addition, our results for $GaCl_3$ and $InCl_3$ fall in the range found by Reedijk and Groenveld,[4] who also note that $TlCl_3$ is non-conducting.

On the basis of i.r.[5] and ^1H n.m.r.[14] studies Schmulbach and Ahmed deduced that the principal species present in acetonitrile solutions of boron trichloride are $[BCl_2(NCMe)_2]^+$ and $[BCl_4]^-$, in the form of ion pairs. However, the electrical-conductivity data show unambiguously that BCl_3 is essentially a non-electrolyte in acetonitrile. If the

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† No reprints available.

principal solute were $[BCl_2(NCMe)_2]^+[BCl_4]^-$ it is difficult to see why this should not behave as a strong 1 : 1 electrolyte. We therefore believe that boron trichloride is present in acetonitrile solution as the molecular adduct $BCl_3{\cdot}MeCN$ (also found from *X*-ray crystallographic studies of the material crystallizing from such solutions [7]).

From the data of Figure 1 it is clear that in acetonitrile aluminium trichloride gives the most highly conducting solutions of the four trichlorides studied. We therefore decided to concentrate the remainder of this research on the aluminium system. In Figure 2 earlier studies of the molar conductivity of solutions of $AlCl_3$ are compared with those obtained in this work. Our results agree quite closely with those of Libus and Puchalska [17] except at very low concentrations where the effect of impurities (notably water) is likely to be greatest. However, the agreement with the work of Graulier [18] and of Schmulbach and Ahmed [5] is poor. From a study of limiting gradients, Libus and Puchalska [17] deduced that a 'complete co-ordination disproportionation' occurred according to equation (3). Such

$$2AlCl_3(s) + 4MeCN \rightleftharpoons [AlCl_2(NCMe)_4]^+ + [AlCl_4]^- \quad (3)$$

deductions are open to question as the experimental results in Figure 3 clearly demonstrate. If the ionization scheme of Libus and Puchalska [17] for a 1 : 1 electrolyte is followed the formula is $[AlCl_2]^+[AlCl_4]^-$ leading to a molecular weight corresponding to Al_2Cl_6. Plotted on this basis the molar conductivity of aluminium trichloride in acetonitrile is indeed similar to that of the 1 : 1 electrolytes $[NMe_4]Cl$ [19] or $[NMe_4][ClO_4]$.[20] If an ionization of the form $[AlCl]^{2+}$-$2[AlCl_4]^-$ is adopted the molecular weight now corresponds to Al_3Cl_9. Replotting the molar conductivity for solutions of aluminium trichloride on this basis gives results closely comparable with those for the 1 : 2 electrolyte $Mg[ClO_4]_2$ as shown in Figure 3. *These experiments thus do not distinguish the electrolyte type or identify the ions present in solution.*

Vibrational Spectroscopy.—The i.r. spectra of solutions of aluminium trichloride in acetonitrile and of the solid which crystallizes from such solutions (empirical formula $AlCl_3{\cdot}2MeCN$) are disappointing. In the region where Al–Cl vibrations might be expected the absorptions are rather broad and largely unresolved. Such studies did not appear to be useful. However, it is worth noting that Jones and Wood [21] from i.r. spectroscopy (largely in the CN stretching region) suggested that the crystalline solid $AlCl_3{\cdot}2MeCN$ contained 'free MeCN' as well as co-ordinated MeCN.

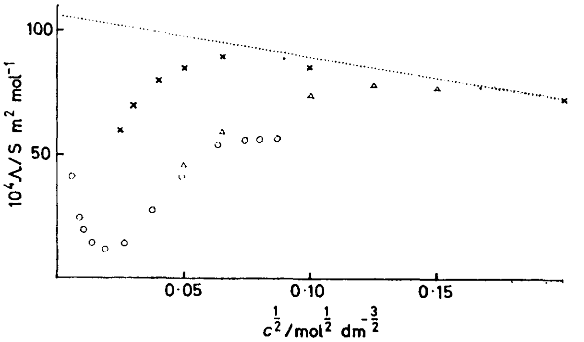


FIGURE 2 Comparison of literature values for the molar conductivity of aluminium trichloride in acetonitrile with this work (– – – –): (○) ref. 5; (×) ref. 17; (△) ref. 18

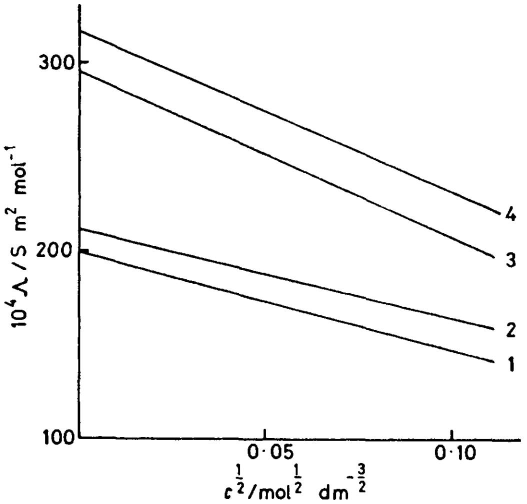


FIGURE 3 Molar conductivity of (1) $[NMe_4][ClO_4]$,[20] (2) $AlCl_3$ formulated as $[AlCl_2]^+[AlCl_4]^-$, (3) $Mg[ClO_4]_2$, and (4) $AlCl_3$ formulated as $[AlCl]^{2+}$, in acetonitrile

As noted by Schmulbach [22] and others the Raman spectra of solutions of aluminium trichloride in acetonitrile and of the solid $AlCl_3{\cdot}2MeCN$ strongly suggest the presence of the $[AlCl_4]^-$ ion. However, the nature of the cation remains obscure although various structures have been proposed, *e.g.* $[Al_2Cl_5{\cdot}n MeCN]^+$,[22] $[AlCl_2(NCMe)_4]^+$,[17] and $[Al(NCMe)_6]^{3+}$.[21] In an attempt to resolve this difficulty we made a semiquantitative Raman study of the effect of adding solid $[NEt_4]Cl$ or LiCl to a solution of $AlCl_3$ in acetonitrile. The integrated intensity of the polarized band at 349 cm^{-1} (assumed to be entirely due to ν_1 of $[AlCl_4]^-$) was measured relative to an adjacent depolarized solvent band at 380 cm^{-1}. The ratio of these two bands was monitored as solid $[NEt_4]Cl$ or LiCl was added to the solution. No correction was made for geometrical optical effects since we did not feel that the results warranted this.[23] Separate experiments showed that: (*a*) using CD_3CN as solvent no peak is observed at 380 cm^{-1}; (*b*) the intensity of ν_1 of $[AlCl_4]^-$ in solutions of $[NEt_4][AlCl_4]$ does not alter (within the limits of our measurements) on addition of solid $[NEt_4]Cl$; (*c*) the measured depolarization ratio of the band at 349 cm^{-1} in solutions of $AlCl_3$ in acetonitrile was effectively zero. The results show that a limiting value for the ratio of the intensities of the bands at 349 and 380 cm^{-1} is reached when the (mole) ratio of the aluminium trichloride to added chloride is 1 : 1. On the basis that the band at 349 cm^{-1} is exclusively due to $[AlCl_4]^-$, the initial ratio (for pure $AlCl_3$) divided by the ratio for complete conversion into $[AlCl_4]^-$ gives the concentration of $[AlCl_4]^-$ initially present in the aluminium trichloride solution. The result obtained from these solutions (0.401, 0.614, and 0.780 mol dm^{-3}) was 68 ± 2%. In another experiment the ratio of the peak areas was measured as a function of the concentration of $AlCl_3$ in the solution, without any addition of chloride ion. The results are summarized in Figure 4, which includes standardization points for solutions of $[NEt_4][AlCl_4]$ or $Li[AlCl_4]$. The ratios of the peak areas for these points have been multiplied by a factor of 2/3 to bring them on to approximately the same scale. These results suggest that 70% of the aluminium in a solution of aluminium trichloride in acetonitrile is present in the form of $[AlCl_4]^-$. This eliminates the proposed scheme $[AlCl_2(NCMe)_4][AlCl_4]$ as the principal ionization since this would yield a figure of 50% for the $[AlCl_4]^-$ concentration. It also eliminates $[Al_2Cl_5{\cdot}n MeCN]^+$, but while favouring the scheme $[AlCl(NCMe)_5]^{2+}2[AlCl_4]^-$ (corresponding to 66.7% $[AlCl_4]^-$) is not sufficiently definitive to *exclude* $[Al(NCMe)_6]^{3+}3[AlCl_4]^-$ (corresponding to 75% $[AlCl_4]^-$) or a series of linked equilibria.

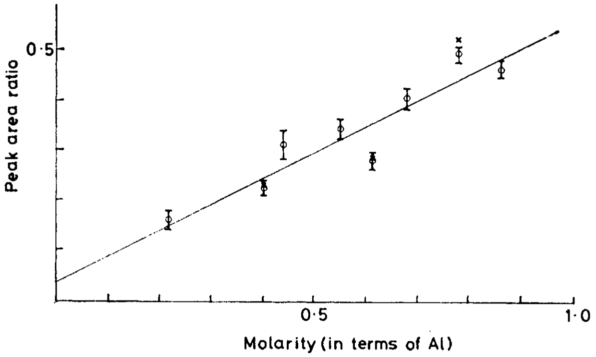


FIGURE 4 Ratio of the peak area for ν_1 of $[AlCl_4]^-$ to that of ν_8 of MeCN plotted as a function of concentration of $AlCl_3$ in solution in acetonitrile. Three points are shown (×) corresponding to solutions of $[NEt_4][AlCl_4]$ or $Li[AlCl_4]$ where the peak-area ratio has been multiplied by 2/3

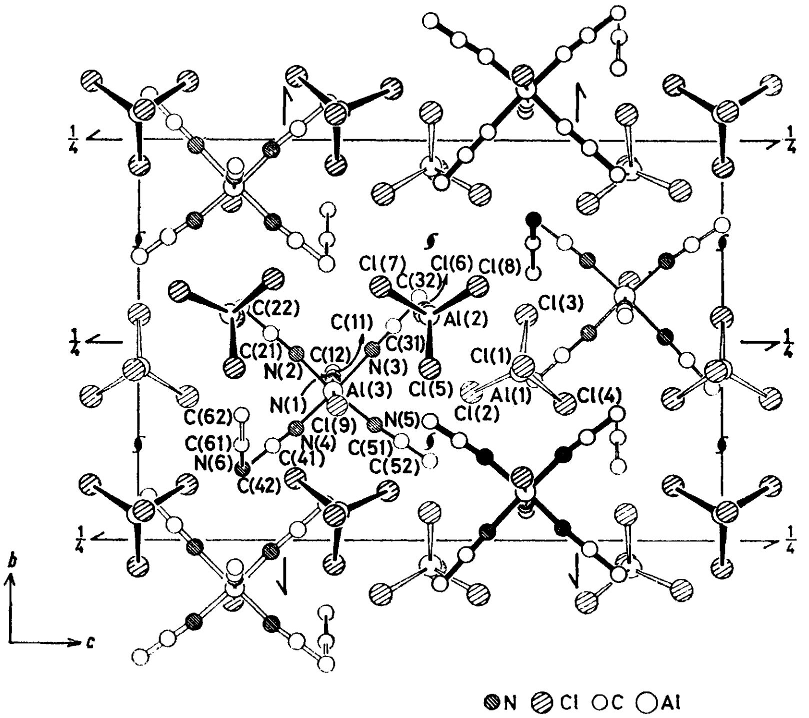


FIGURE 5 A view of the contents of the unit cell projected on the *bc* plane, viewed along the $-x$ axis towards the origin, and showing the crystallographic numbering scheme

It was clear that a means of characterizing the cation was still essential. Since it is known that $[AlCl_4]^-$ gives a narrow ^{27}Al resonance we decided to carry out a quantitative ^{27}Al magnetic resonance study of solutions of $AlCl_3$ in acetonitrile using Fourier-transform techniques. However, before this work was initiated the *X*-ray crystal structure was solved.[24]

X-*Ray Crystal Structure*.—The structure identifies the cation $[AlCl(NCMe)_5]^{2+}$ for the first time and contains the expected anion $[AlCl_4]^-$. In addition there are four molecules of acetonitrile of solvation in the unit cell {which contains four formula units $[AlCl(NCMe)_5][AlCl_4]_2$} as shown in Figure 5 (see also Table 1). The anions have approximate tetrahedral geometry, with a mean Al–Cl separation of 2.119(10) Å and mean Cl–Al–Cl angle of 109.5(5)° (Table 2). The range of Al–Cl distances [2.109(6)—2.141(5) Å] is not unusual, comparing closely with previously observed values for the $[AlCl_4]^-$ ion.[25-27] However, the Al–Cl separation in the octahedrally co-ordinated cation is significantly larger [2.196(4) Å]. This is not unexpected in view of the change in co-ordination number. For example, in the complex ion *cis*-$[AlCl_2(bipy)_2]^+$ (bipy = 2,2′-bipyridyl) the Al–Cl distance[28] is 2.255(2) Å, the increase over that in $[AlCl(NCMe)_5]^{2+}$ resulting from a combination of the strong *trans*-nitrogen donors and the decreased positive charge on the ion. A similar effect is seen in the Al–N distances of the acetonitrile ligand. The four ligands in the plane perpendicular to Al(3)–Cl(9) show a mean Al–N distance of 1.986(11) Å while the unique acetonitrile ligand *trans* to chlorine shows a (greater) distance of 2.021(8) Å. Again this is similar to the behaviour of the Al–N distances in *cis*-$[AlCl_2(bipy)_2]^+$ where those *trans* to Cl at 2.040(3) Å are longer than the distances found when the two nitrogen ligands are *trans* to one another, 2.025(3) Å. Another feature of interest in the cation $[AlCl(NCMe)_5]^{2+}$ is that the four equatorial acetonitrile ligands in the plane perpendicular to Al(3)–Cl(9) bend away from the single chlorine atom giving a mean Cl–Al–N angle of 94.3(6)°. This may be accounted for on the basis of steric effects.

It is difficult to comment on the C–N and C–C distances in the free and bound acetonitrile because of the rather large standard deviations. The values of 1.157(15) and 1.443(17) Å for the C–N and C–C distances in the solvate molecule are very close to those in gaseous acetonitrile (1.157 and 1.458 Å).[29] Some rather careful work[7] on BF_3·MeCN and BCl_3·MeCN gave the co-ordinated acetonitrile C–N and C–C distances as 1.135(5) and 1.439(5) Å and 1.122(7) and 1.437(8) Å respectively. It was however still noted that the differences in the C–N distances for the two compounds were less than twice the standard error. In another recent paper[30] on $[Ni(NCMe)_6][ZnCl_4]$ widely differing C–N and C–C distances were reported for the individual ligand molecules, with a standard deviation ranging from 0.019 to 0.026 in the case of C–N distances and from 0.022 to 0.032 Å for the C–C distances. However, the mean values were given as 1.123(6) Å for the C–N distance and 1.467(8) Å for the C–C distance. These values are also quite close to those found in $BeCl_2$·2MeCN[10] [C–N 1.131(2) and C–C 1.439(3) Å] and for $VOCl_3$·MeCN[31] [C–N 1.137(2) and C–C 1.445(3) Å]. On the basis of the above brief discussion we prefer not to comment on the distances observed here, but merely to note that they are unexceptional. There are

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Al(1)	0.494 0(3)	0.429 8(2)	0.656 5(1)
Cl(1)	0.284 7(2)	0.437 1(2)	0.662 9(2)
Cl(2)	0.554 0(5)	0.375 7(3)	0.568 0(2)
Cl(3)	0.575 7(3)	0.563 5(3)	0.666 2(1)
Cl(4)	0.563 2(4)	0.346 6(4)	0.731 4(2)
Al(2)	0.007 0(3)	0.571 1(2)	0.497 1(1)
Cl(5)	0.939 7(4)	0.431 7(2)	0.497 9(1)
Cl(6)	0.215 1(3)	0.573 6(3)	0.490 8(2)
Cl(7)	0.929 2(4)	0.636 7(3)	0.415 5(2)
Cl(8)	0.936 5(4)	0.634 4(3)	0.580 9(2)
Al(3)	0.623 9(2)	0.378 0(2)	0.336 1(1)
Cl(9)	0.412 8(2)	0.343 5(2)	0.339 4(1)
N(1)	0.819 5(7)	0.405 9(5)	0.333 8(4)
C(11)	0.929 0(9)	0.415 4(7)	0.331 8(4)
C(12)	0.076 3(9)	0.424 2(10)	0.329 5(5)
N(2)	0.606 1(8)	0.468 3(5)	0.266 8(3)
C(21)	0.597 9(9)	0.519 6(6)	0.226 5(4)
C(22)	0.587 8(11)	0.586 2(6)	0.174 3(5)
N(3)	0.607 4(8)	0.478 3(5)	0.399 7(3)
C(31)	0.597 0(9)	0.535 6(7)	0.434 6(4)
C(32)	0.583 3(12)	0.611 3(8)	0.480 5(5)
N(4)	0.666 6(8)	0.284 6(6)	0.270 6(3)
C(41)	0.699 1(10)	0.240 1(7)	0.229 6(4)
C(42)	0.742 3(13)	0.182 1(9)	0.175 5(5)
N(5)	0.672 2(8)	0.291 5(6)	0.406 2(3)
C(51)	0.706 8(10)	0.249 6(7)	0.448 3(4)
C(52)	0.749 6(12)	0.196 6(9)	0.502 8(5)
N(6)	0.418 8(11)	0.180 1(7)	0.177 8(5)
C(61)	0.345 6(12)	0.240 9(7)	0.174 3(5)
C(62)	0.254 7(14)	0.316 9(8)	0.169 4(7)

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

(*i*) Anions

Al(1)–Cl(1)	2.125(4)	Al(2)–Cl(5)	2.141(5)
Al(1)–Cl(2)	2.113(5)	Al(2)–Cl(6)	2.111(5)
Al(1)–Cl(3)	2.124(5)	Al(2)–Cl(7)	2.117(5)
Al(1)–Cl(4)	2.109(6)	Al(2)–Cl(8)	2.115(5)

(*ii*) Cation

Al(3)–Cl(9)	2.196(4)	Al(3)–N(1)	2.021(8)
N(1)–C(11)	1.117(12)	C(11)–C(12)	1.497(14)
Al(3)–N(2)	1.973(8)	Al(3)–N(3)	1.988(8)
N(2)–C(21)	1.134(12)	N(3)–C(31)	1.117(12)
C(21)–C(22)	1.469(13)	C(31)–C(32)	1.472(15)
Al(3)–N(4)	1.984(8)	Al(3)–N(5)	1.999(8)
N(4)–C(41)	1.129(13)	N(5)–C(51)	1.133(12)
C(41)–C(42)	1.484(16)	C(51)–C(52)	1.448(15)

(*iii*) Solvent

N(6)–C(61)	1.157(15)	C(61)–C(62)	1.443(17)

(*b*) Angles

(*i*) Anions

Cl(1)–Al(1)–Cl(2)	111.1(2)	Cl(5)–Al(2)–Cl(6)	109.5(2)
Cl(1)–Al(1)–Cl(3)	109.7(2)	Cl(5)–Al(2)–Cl(7)	108.4(2)
Cl(1)–Al(1)–Cl(4)	108.2(2)	Cl(5)–Al(2)–Cl(8)	107.4(2)
Cl(2)–Al(1)–Cl(3)	108.3(2)	Cl(6)–Al(2)–Cl(7)	108.2(2)
Cl(2)–Al(1)–Cl(4)	110.5(2)	Cl(6)–Al(2)–Cl(8)	112.4(2)
Cl(3)–Al(1)–Cl(4)	109.0(2)	Cl(7)–Al(2)–Cl(8)	110.8(2)

(*ii*) Cation

Cl(9)–Al(3)–N(1)	178.3(3)	N(1)–Al(3)–N(5)	84.6(3)
Cl(9)–Al(3)–N(2)	95.0(3)	N(2)–Al(3)–N(3)	90.0(3)
Cl(9)–Al(3)–N(3)	93.7(3)	N(2)–Al(3)–N(4)	87.8(3)
Cl(9)–Al(3)–N(4)	94.4(3)	N(2)–Al(3)–N(5)	171.0(4)
Cl(9)–Al(3)–N(5)	94.0(3)	N(3)–Al(3)–N(4)	171.7(3)
N(1)–Al(3)–N(2)	86.4(3)	N(3)–Al(3)–N(5)	89.3(3)
N(1)–Al(3)–N(3)	87.2(3)	N(4)–Al(3)–N(5)	91.6(3)
N(1)–Al(3)–N(4)	84.7(3)		
Al(3)–N(1)–C(11)	175.4(8)	N(1)–C(11)–C(12)	177.8(11)
Al(3)–N(2)–C(21)	178.8(8)	N(2)–C(21)–C(22)	179.8(10)
Al(3)–N(3)–C(31)	178.8(8)	N(3)–C(31)–C(32)	179.8(11)
Al(3)–N(4)–C(41)	171.3(8)	N(4)–C(41)–C(42)	179.7(11)
Al(3)–N(5)–C(51)	173.1(8)	N(5)–C(51)–C(52)	179.1(11)

(*iii*) Solvent

N(6)–C(61)–C(62)	179.6(12)

TABLE 3

Results of ^{27}Al n.m.r. studies on acetonitrile solutions

Sample	Molarity (by weight)	Molarity by integral trace		$[AlCl_4^-]$ divided by total Al molarity	Resonances (p.p.m.) observed [a] in addition to $[AlCl_4]^-$ [b]
		$[AlCl_4]^-$	'octahedral Al'		
$AlCl_3$	0.089 3	0.061 7	0.027 6	0.69	14.0, 23.0
	0.200	0.133	0.067	0.665	14.0, 23.0
	0.395	0.280	0.115	0.709	14.0, 23.0, 33.0
	0.631	0.452	0.179	0.716	14.0, 23.0, 33.0
	0.931	0.647	0.284	0.695	14.0, 23.0, 33.0
$[AlCl_4]^-$	0.098 5	0.095 8	0.002 75		23.0 [c]
	0.623	0.589	0.034		23.0 [c]
	0.963	0.892	0.071 3		23.0 [c]
	0.098 5 [d]	0.098 5	0		
	0.623 [d]	0.623	0		
	0.963 [d]	0.963	0		

[a] In all cases the peak at 23.0 p.p.m. dominated these spectra. [b] $[AlCl_4]^-$ appeared at −102 p.p.m. from $[Al(OH_2)_6]^{3+}$, the negative sign indicating a low-field shift. [c] Trace amount of $[AlCl_3Br]^-$ at −98.4 p.p.m. [d] Contains excess of Cl^- over $[AlCl_4]^-$.

no significantly short intramolecular distances and the solvent molecule has no contact distance shorter than 3.09(1) Å.

N.M.R. Spectra.—Several ^{27}Al (refs. 32—34) and ^{1}H (refs. 14, 32, and 35) magnetic resonance studies have been made of aluminium salts dissolved in acetonitrile. *Total* solvation numbers can be obtained by ^{1}H n.m.r. spectroscopy and are found to be quite small (*h* 1.5) for aluminium trichloride solutions, but larger for Al[ClO$_4$]$_3$ solutions, where the latest studies suggest a value of *ca.* 5.[36] Since the Al^{3+} ion is known to be hexasolvated by many solvents, these values for *h* imply the presence of unsolvated or partially solvated species in these solutions.

Previous work [32] on ^{27}Al magnetic resonances in solutions of AlCl$_3$ in acetonitrile has shown the presence of both octahedral and tetrahedral species (predominantly [AlCl$_4$]$^-$). The resonance in the octahedral region was originally believed to be a singlet, understandably so since spectra were obtained in the derivative mode so that fine detail would be obscured by the finite field-modulation amplitude which has to be used. This singlet was quite reasonably assigned to the ion [Al(NCMe)$_6$]$^{3+}$. Recent Fourier-transform spectra,[34] together with those reported here, show fine structure and enable more rigorous assignments to be made.

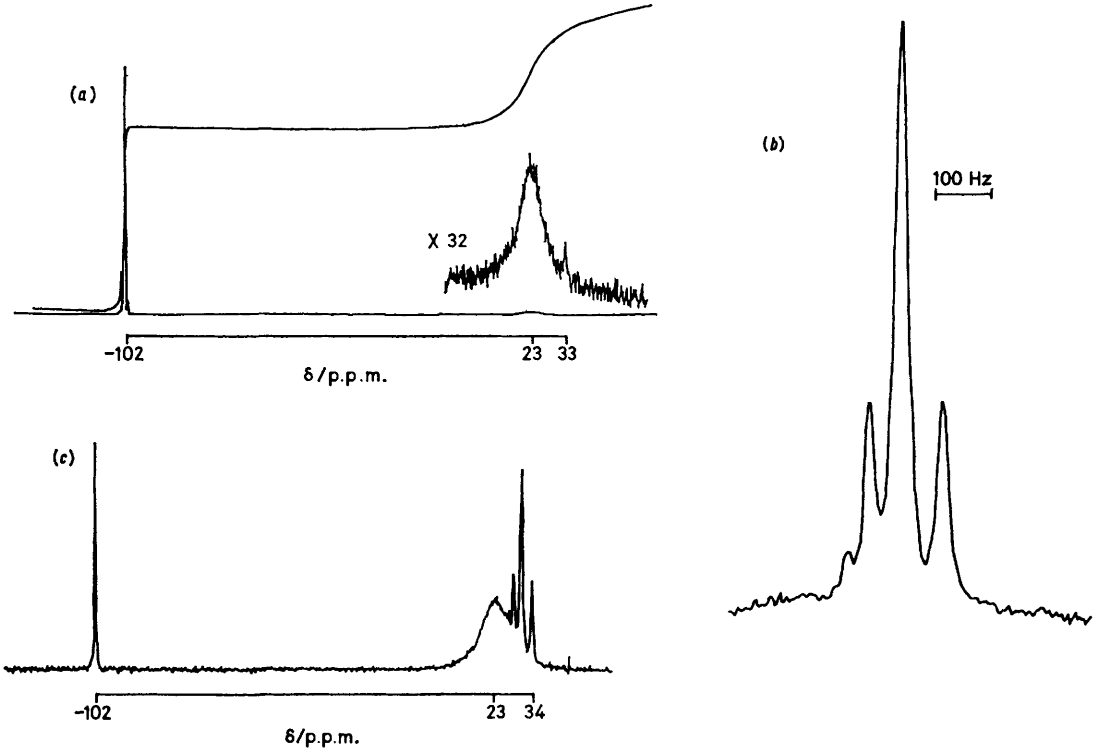


FIGURE 6 The ^{27}Al n.m.r. spectrum in acetonitrile of (*a*) AlCl$_3$, (*b*) Al[ClO$_4$]$_3$, and (*c*) AlCl[ClO$_4$]$_2$

Aluminium-27 n.m.r. spectra were obtained for a variety of solutions and the detailed results are reported in Table 3. These observations may be summarized as follows: (*a*) [NEt$_4$][AlCl$_4$] solutions containing a large excess of [NEt$_4$]Cl showed only resonances due to [AlCl$_4$]$^-$ at all concentrations studied; (*b*) one solution of [NEt$_4$][AlCl$_4$] containing a 5 mol % excess of [NEt$_4$]Cl over the stoicheiometric composition showed only [AlCl$_4$]$^-$; (*c*) [NEt$_4$][AlCl$_4$] solutions at several concentrations showed mainly [AlCl$_4$]$^-$ with small quantities of octahedral species having broad resonances. (The presence of detectable octahedral species in these solutions could be due to the fact that they are not strictly stoicheiometric, a small deficit of [NEt$_4$]Cl having occurred in making up the supposedly 1 : 1 [NEt$_4$]Cl : AlCl$_3$ mixture on a vacuum line); (*d*) aluminium trichloride at several concentrations showed the presence of [AlCl$_4$]$^-$ and of octahedral species [Figure 6(*a*)]; (*e*) Al[ClO$_4$]$_3$ contained only octahedral species and showed five remarkably sharp lines [Figure 6(*b*)]; (*f*) AlCl[ClO$_4$]$_2$ gave a spectrum containing features of both (*d*) and (*e*), as shown in Figure 6(*c*).

Chlorine-35 n.m.r. studies of a 0.127 mol dm^{-3} solution of [NEt$_4$]Cl in acetonitrile showed a single line shifted 40 p.p.m. downfield from that of a dilute aqueous solution of sodium chloride. Acetonitrile solutions of AlCl$_3$ (0.20 and 0.631 mol dm^{-3}) and of [NEt$_4$][AlCl$_4$] (0.623 mol dm^{-3}) gave no evidence of a (sharp) resonance due to chloride ion. The signal-to-noise ratio of the original [NEt$_4$]Cl solutions suggested that a concentration of 0.001 mol dm^{-3} chloride ion would have been detectable. On the basis that the non-observation of a signal is not due to a fast exchange process, we shall assume that the chloride-ion concentration in our solutions is negligible.

To understand the ^{27}Al spectra it is necessary to consider both the composition of the solutions and the widths of the resonances. For the aluminium trichloride solutions containing no [NEt$_4$]Cl the [AlCl$_4$]$^-$ peak area as a proportion of the total aluminium by integration had a mean value of 0.695 with all results lying within the limits $+0.021$ to -0.030. The agreement with the results of the Raman experiment is excellent.

In all the solutions of AlCl$_3$ in acetonitrile studied by ^{27}Al n.m.r. spectroscopy the principal resonance in the octahedral region lay at a shift of $+23.0$ p.p.m. and was more than 20 times as broad as the $[AlCl_4]^-$ resonance. Bearing in mind the lack of free Cl^-, the fact that 69.5% of the aluminium is present as $[AlCl_4]^-$, and the broadness of the main peak in the octahedral region, we assign this feature to the $[AlCl(NCMe)_5]^{2+}$ ion. The weak sharp feature at *ca.* 33 p.p.m. would then be due to a small amount of the hexasolvate $[Al(NCMe)_6]^{3+}$.

Confirmation of these assignments comes from studies of solutions of stoicheiometry $Al[ClO_4]_3$ and $AlCl[ClO_4]_2$, obtained by adding silver perchlorate to solutions of $AlCl_3$ in acetonitrile. (In all cases the precipitated AgCl was weighed and shown to correspond to complete conversion of the perchlorate salt into the chloride salt.) The $Al[ClO_4]_3$ solution had a spectrum consisting of five unequally spaced sharp resonances. This demonstrates that perchlorate ion interacts strongly with Al^{3+} in such solutions. The number of different species and the sharpness of the lines are both surprising. However, violations of the general rule that non-symmetrical complexes of a quadrupolar nucleus should have broad lines are now well documented for ^{27}Al.

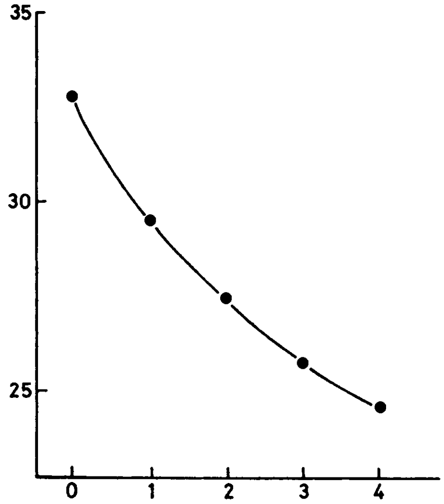


FIGURE 7 Plot of ^{27}Al n.m.r. shift for the five lines in the perchlorate spectrum against an arbitrary linear scale

These resonances were also present in the $AlCl[ClO_4]_2$ solution, overlying the broad 23 p.p.m. resonance, some $[AlCl_4]^-$ being observed to low field. Approximately 75% of the aluminium is present in the band at 23 p.p.m. and 6.1 ± 0.4% in the $[AlCl_4]^-$, the rest being in the sharp peaks in the octahedral region. On the basis that the last peaks are due to aluminium species not containing chloride, and that there is no free chloride ion present, then the formula of the species responsible for the peak at 23 p.p.m. is calculated to be $[AlCl]^{2+}$.

The method of assignment of the highest-field sharp peak to $[Al(NCMe)_6]^{3+}$ is of interest since it is surprising that so little is present in the $AlCl_3$ solutions and even in the $Al[ClO_4]_3$ solutions it is not the major species. The chemical-shift measurements, while indicative, are not conclusive because of susceptibility effects and the lack of spectrometer lock. If we use $[AlCl_4]^-$ as a secondary (unproven) internal standard (shift taken as −102 p.p.m. in all samples) we find that in the $AlCl[ClO_4]_2$ solution the peaks occur at 23.0, 23.6 (trace), 24.8, 28.5, 30.7 (most intense, sharp peak), and 34.0 p.p.m. The corresponding, externally standardized, values for $Al[ClO_4]_3$ are 24.5 (trace), 25.7, 27.4, 29.5 (most intense), and 32.8 p.p.m. If we plot the last values against a linear scale, which may be read as relating to the number of ' complexed ' perchlorate ions (Figure 7), we obtain a regular curve which suggests that we have a set of ' complexes ' with the highest field one being the hexasolvate. This, the sharpness of the lines, and the closeness of the chemical shifts of the hexasolvate lines in the three types of solution make any other assignment very difficult to justify. The assignment may also be considered to be in accord with the average solvation number of Al^{3+} in $Al[ClO_4]_3$ being 5.

The whole of these data then is self-consistent, is in agreement with the Raman and conductivity results, and shows that the major species present in solutions of aluminium trichloride in acetonitrile are identical to those found in the solid-state *X*-ray diffraction investigation. There is no evidence for the occurrence of $AlCl_3{\cdot}MeCN$ or for the formation of chlorine-bridged species. Finally, it may be noted that the deduction of solvation numbers by ^1H n.m.r. studies relies on measurement of the relative areas for ' bound ' and ' free ' acetonitrile. As noted above, the average solvation number found experimentally for aluminium trichloride solutions is close to 1.5.[35] For the ionization scheme $4AlCl_3 \longrightarrow Al^{3+} + 3[AlCl_4]^-$ this gives a solvation number of six for the Al^{3+} ion. For the ionization scheme proposed here [equation (4)] the solvation number

$$3AlCl_3 \longrightarrow [AlCl]^{2+} + 2[AlCl_4]^- \qquad (4)$$

becomes 4.5 for the $[AlCl]^{2+}$ ion, close to that required by the formulation $[AlCl(NCMe)_5]^{2+}$, and well within the usual error limits of such determinations.

DISCUSSION

The behaviour of a species such as aluminium trichloride in a solvent is governed by many factors and only an elementary discussion is possible. Perhaps the most important features will be the donor power of the solvent, the dielectric constant of the solvent, and the co-ordination number of the metal. The results obtained here demonstrate that acetonitrile is not able to displace Cl^- from $[AlCl_4]^-$ to any appreciable extent. It is reasonable to assume that the Al^{3+} ion would have a co-ordination number of six in acetonitrile. Silicon tetrachloride (isoelectronic with $[AlCl_4]^-$) will not co-ordinate acetonitrile or readily add chloride ions.[37] The compound $BCl_3{\cdot}MeCN$ is molecular in acetonitrile.

By analogy with $SiCl_4$, the hypothetical molecule $AlCl_3{\cdot}MeCN$ would not be expected to accept further acetonitrile molecules. Similarly, by analogy with $BCl_3{\cdot}MeCN$, it would be expected to be molecular in acetonitrile. The driving force for reaction (5) is

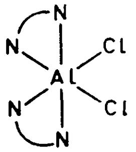
$$3(AlCl_3{\cdot}MeCN) + 2MeCN \longrightarrow [AlCl(NCMe)_5]^{2+} + 2[AlCl_4]^- \qquad (5)$$

therefore most likely to be the change in co-ordination number from four in $[AlCl_4]^-$ or $AlCl_3{\cdot}MeCN$ to six for $[AlCl(NCMe)_5]^{2+}$. Clearly the further step in ionization (6) requires the removal of a Cl^- from a doubly charged

$$4[AlCl(NCMe)_5]^{2+} + 8[AlCl_4]^- \longrightarrow 3[Al(NCMe)_6]^{3+} + 9[AlCl_4]^- + 2MeCN \qquad (6)$$

ion and a decrease in co-ordination number for the aluminium.

A recent X-ray diffraction determination of the structure of the compound obtained by adding $AlCl_3$ in acetonitrile to 2,2′-bipyridyl (bipy) in the same solvent is of interest.[28] The formula found is $[AlCl_2(bipy)_2]Cl\cdot MeCN$. It may at first sight appear that this conflicts with the above discussion. However, we note that powerful donors such as pyridine or bipy can displace Cl^- from $[AlCl_4]^-$. The formation of $[AlCl_4]^-$ in the presence of these donors is thus not to be expected. Similarly the ion contains four strongly donating nitrogen ligands. Ionization of two more chloride ions to give a triply charged complex ion is necessary to add one more bipy and, further, there is no increase in the co-ordination number.



$\widehat{NN}$ = 2,2′-bipyridyl

EXPERIMENTAL

Acetonitrile was dried and purified as described previously.[2] The trichlorides of Al, Ga, and In were prepared from high-purity metals by chlorination, followed by sublimation *in vacuo* into glass ampoules fitted with breakseals. Commercial boron trichloride (B.D.H.) was distilled *in vacuo*. With the exception of the handling of BCl_3 (when greaseless taps were used), operations were carried out in an all-glass vacuum line using no taps or joints. The apparatus to be used was flamed out prior to sealing off for the experimental study. Solvent volumes were measured using calibrated burettes. Weights of aluminium, gallium, or indium trichloride were obtained by subliming the material into an ampoule with a fragile tip, a constriction then being sealed to allow removal of the ampoule from the vacuum line. The ampoule was weighed, the tip broken *in vacuo*, the trichloride sublimed out into a breakseal ampoule, and the residual glass weighed to give the weight of material after a buoyancy correction. Boron trichloride was transferred quantitatively by means of calibrated volumes, measuring pressures by use of mercury manometers. Solutions were analyzed gravimetrically for total chloride (as silver chloride) at the termination of experiments. Weighed amounts of dry tetraethylammonium chloride, lithium chloride, or silver perchlorate were dried at 120 °C *in vacuo, in situ*.

Conductance measurements were made using a glass cell with lightly platinized platinum electrodes sealed through the glass by means of a thin platinum foil.[2,38] The cell was held at 25 °C and arrangements were made to stir the solution periodically. Typical cell constants were of the order of 8.5 m^{-1}. Samples for Raman (using a Cary 82 or Spex 1401 Raman spectrometer and Spectra Physics 170 argon-ion laser excitation) and n.m.r. studies were made up using vacuum-line techniques. Aluminium-27 n.m.r. spectra were obtained at 23.45 MHz using a Bruker HFX3 spectrometer in the Fourier-transform mode with an external standard. Where quantitative data were required a relatively slow pulse repetition rate of 1.53 s^{-1} was used to avoid saturation of the narrow resonances. Integrations were carried out in the standard way and no lock was used. Colourless crystals of $AlCl_3\cdot 2MeCN$ were obtained by dissolving $AlCl_3$ in an excess of acetonitrile *in vacuo*, and allowing crystallization in a sealed ampoule. The data crystal was mounted in a Lindemann glass tube using dry-box techniques.

Crystal Data.—$C_{12}H_{18}Al_3Cl_9N_6$, $M = 646.3$, Orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 10.121(6)$, $b = 14.562(13)$, $c = 21.055(13)$ Å, $D_m = 1.37$ g cm^{-3}, $Z = 4$, $D_c = 1.38$ g cm^{-3}, $F(000) = 1\ 296$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 9.18 cm^{-1}. Diffracted intensities were collected at room temperature on an automatic Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$, according to methods discussed earlier.[39] 3 117 Reflections were corrected for Lorentz and polarization effects, but not for X-ray absorption. No significant decay in the intensities of the standard reflections was recorded during the period of data collection (56 h). All the data were used in the solution of the structure, but the final refinements were carried out using only those intensities (2 355) with $I \geqslant 2.5\sigma(I)$, $\sigma(I)$ being the error in the observed intensity based on counting statistics alone.

Solution and Refinement of the Structure.—Severe overlap in the Patterson function resulted in the failure of conventional heavy-atom methods and solution was achieved by direct methods. Twelve Σ_1 relationships with $P^+ \geqslant 0.99$, three origin-defining reflections, and two symbols (a,b) in a symbolic addition procedure yielded 63 phases and removed the ambiguities of a and b; b was used to define the enantiomorph. This starting set of phases was tangent-refined to give phases for all $|E_h| \geqslant 1.3$. The resulting E map exhibited high pseudosymmetry, for example 2_1 axes behaving as mirror planes, but by inspection it was possible to estimate the two most likely independent $[AlCl_4]^-$ groups, together with probable 'Al–Cl' octahedral fragments. Phasing on the tetrahedra alone confirmed their correct positions and the remaining atoms were located from an electron-density difference synthesis. The peculiarities of the Patterson synthesis and the strong Σ_1 relationships could then be explained.

Atomic scattering factors for C, N, and Cl[40] and for Al[41] were taken from the literature, those for Al and Cl being corrected for the effects of anomalous dispersion (Al: $\Delta f' = 0.056$, $\Delta f'' = 0.052$; Cl: $\Delta f' = 0.132$, $\Delta f'' = 0.159$). Weights were applied according to the scheme $w = 1/(a + b|F_o| + c|F_o|^2)$ where $a = 1.46$, $b = -0.013\ 5$, and $c = 0.000\ 45$. a, b, and c were chosen from an analysis of $w\Delta^2$ with F_o and $\sin\theta$; $\Delta = |F_o - F_c|$. The structure was refined by block-diagonal least-squares techniques. Refinement converged at $R = 0.061$ (R' 0.074) for 2 355 reflections and 272 refined parameters, with a maximum shift-to-error ratio of 0.04. A final difference electron-density synthesis showed no peaks >0.4 and < -0.2 e Å^{-3}. Hydrogen atoms were not included in the calculation.

Final fractional positional parameters are given in Table 1 and molecular parameters in Table 2. Calculations were carried out at the University of London Computing Centre using the 'X-RAY' system of programs,[42] after initial computation at Glasgow University using MULTAN.[43] Observed and calculated structure factors and all anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22401 (16 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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