Inorg. Chem. **1982**, *21*, 2241–2246

Contribution from the Laboratoire de Spectroscopie Infrarouge, Associé au CNRS, L.A. 124,
University of Bordeaux I, 33405 Talence Cedex, France, and the University of Rouen, 76130 Mont Saint-Aignan, France

Spectroscopic Investigations of Complexes between Acetonitrile and Aluminum Trichloride. 2. Study of $AlCl_3$ in Acetonitrile Mixtures of Tetramethylammonium Chloride, Water, or Nitromethane

M. DALIBART,*[1a] J. DEROUAULT,[1a] and P. GRANGER[1b]

Received July 22, 1981

This study concerns the competition between acetonitrile and three other ligands with respect to complex formation with aluminum chloride. Numerous mixed species are formed. The $AlCl_3/CH_3CN/N(CH_3)_4Cl$ and $AlCl_3/CH_3CN/H_2O$ systems are ionic. In the $AlCl_3/CH_3CN/CH_3NO_2$ system, neutral and ionic complexes are in equilibrium; the analysis of this system is based on infrared, Raman, and Al NMR studies of CH_3NO_2 solutions of $AlCl_3$ and $AlBr_3$. All the complex species have been identified by using on one hand the method previously described and on the other hand semiempirical models in order to determine the chemical shift and the line width of the Al NMR signals.

Introduction

The preceding paper was devoted to the study of binary solutions of $AlCl_3$ in CH_3CN: the ratio $R = [CH_3CN]/[AlCl_3]$ was modified in the range of 5.6–37.4 whereas the ratio $[Cl^-]/[Al^{3+}] = 3$ was not varied.[2] The analysis of ternary solutions $AlCl_3/CH_3CN/N(CH_3)_4Cl$ allows us to investigate the influence of the variation of the $[Cl^-]/[Al^{3+}]$ relative concentration. In an earlier paper, Hon[3] had shown that the addition of LiCl to a solution of $AlCl_3$ in CH_3CN provides Cl^- anions which displace bound CH_3CN and lead to the unique aluminum species $AlCl_4^-$. Nevertheless, Hon assumed that $Al(CH_3CN)_6^{3+}$ was the only cationic species before the addition of LiCl and gave no identification about the intermediate species involved in the substitution reaction. This study is now feasible by recording the Al NMR spectra of ternary solutions and by using our previous Al NMR data concerning the binary solutions.

On the other hand, the analysis of ternary solutions $AlCl_3/CH_3CN/L'$, in which L′ is another Lewis base, would provide a better knowledge of the coordination properties of the aluminum atom.

Attempts to predict the result of the competition between two Lewis bases have been made by considering the value of the dissociation energy of 1:1 adducts. In the earlier DN system, derived by Gutman,[4] only one Lewis acid ($SbCl_5$) was taken as a common reference for all addition reactions with the various Lewis bases. A more accurate E/C system, in which properties of both the acid and the base have been taken into account, was derived later by Drago.[5] When the investigated reactions are more complicated than the simple formation of a 1:1 adduct, such predictions become quite difficult since each intermediate complex AB_n should be considered as the Lewis acid in the reaction

$$AB_n + L' \rightleftarrows AB_nL'$$

Thus the preceding systems may be used with great discretion, and one may only conclude that the complexes formed by the base with the greater DN value will be probably more stable. Consequently, we have investigated the influence of CH_3NO_2 and H_2O (of which the DN values are lower (DN = 2.7) and higher (DN = 18) respectively) on CH_3CN (DN = 14.1) solutions of $AlCl_3$. Among the commonly used Lewis bases with lower DN values, CH_3NO_2 has been selected because complexes formed after substitution are soluble in CH_3NO_2/CH_3CN mixtures. On the other hand, when experiments are carried out under common experimental conditions, water may often interfer in the reactions and a number of works have been devoted in the past to the ^1H NMR study of the competition between water and other Lewis bases with respect to aluminum salts.[6–9] Since the $AlCl_3/CH_3CN/H_2O$ system has not been investigated, Al NMR data related to this system will be of interest.

The interpretation of the Al NMR spectra of such mixtures will be carried out on the basis of previous Al NMR data and on the results of pairwise interactions and point-charge models. In the case of CH_3NO_2, we will investigate with vibrational infrared and Raman spectroscopy the 1:1 $AlX_3{\cdot}CH_3NO_2$ solid compounds (X = Cl and Br) in order to compare their spectra to those of solutions.

Experimental Section

The solutions have been prepared according to the previously described methods.[2,10]

^{27}Al NMR spectra have been recorded on a Bruker WH 90 C at 23.45 MHz or on a Bruker WH 250 at 65.14 MHz when available. ^{35}Cl NMR spectra were recorded on the WH 90 C instrument at 8.82 MHz. The procedure used to collect and to process the FID has been described in the preceding papers as well as the correction method applied to the integration measurements.[2,10] All chemical shifts are measured from $Al(H_2O)_6^{3+}$, which is taken as an external reference. The proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer; the internal reference was the upfield ^{13}C satellite of CH_3NO_2. Infrared data were obtained with a Perkin-Elmer 180 instrument in the range of 600–200 cm^{-1} and with a Polytec FIR 30 interferometer in the range of 500–50 cm^{-1}. Solid samples were analyzed as mulls in Nujol or hexachlorobutadiene. Raman spectra were recorded with a Coderg T 800 triple monochromator powered by an Ar^+ Spectra-Physics laser tuned at 488 nm. The resolution was about 3 cm^{-1} in both spectroscopies.

Results and Discussion

I. $AlCl_3/CH_3CN/N(CH_3)_4Cl$ Mixtures. We have analyzed a number of ternary solutions ($AlCl_3/CH_3CN/N(CH_3)_4Cl$). The value of the molar ratio $R = [CH_3CN]/[AlCl_3]$ was 6.5 for each mixture and the ratio $r = [N(CH_3)_4Cl]/[AlCl_3]$ was varied in the range of 0–1.[11] Previous results related to

---

(1) (a) University of Bordeaux. (b) University of Rouen.
(2) M. Dalibart, J. Derouault, P. Granger, and S. Chapelle, *Inorg. Chem.*, **21**, 1040 (1982).
(3) J. F. Hon, *Mol. Phys.*, **15**, 57 (1968).
(4) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York, 1968.
(5) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973).
(6) A. Fratiello and R. Schuster, *Tetrahedron Lett.* **46**, 4641 (1967); A. Fratiello, R. E. Lee, V. M. Nishida, and R. Schuster, *J. Chem. Phys.*, **47**, 4951 (1967); *Inorg. Chem.*, **8**, 69 (1969).
(7) S. Thomas, and W. L. Reynolds, *Inorg. Chem.*, **9**, 78 (1970).
(8) D. P. Olander, R. S. Marianelli, and R. C. Larson, *Anal. Chem.*, **41**, 1097 (1976).
(9) Y. Ruben and J. Reuben, *J. Phys. Chem.*, **80**, 2394 (1976).
(10) M. Dalibart, J. Derouault, and P. Granger, *Inorg. Chem.*, **20**, 3975 (1981).

0020-1669/82/1321-2241$01.25/0

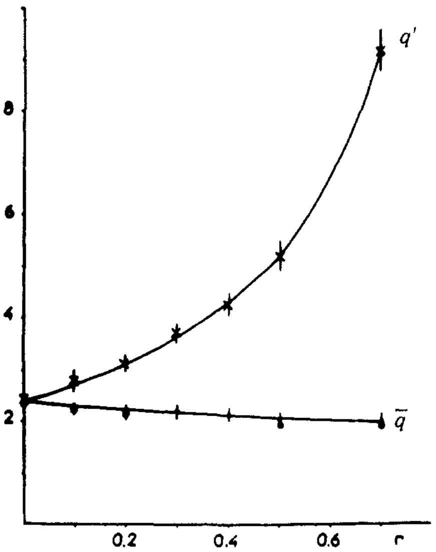

Figure 1. Effect of the addition of Cl^- in a CH_3CN solution of $AlCl_3$: ×, q' (with uncertainty); ●, experimental average ionic charge $\bar{q}$ (with uncertainty); ○, calculated average charge from simulated spectra with $q_A = 3$, $q_B = 2$, $q_C = 1$, $q_D = 3$, and $q_E = 0$.

CH_3CN solutions of $AlCl_3$ had shown that, in addition to the $AlCl_4^-$ anion, four cations are formed: $Al(CH_3CN)_5^{3+}$ (D, −10 ppm), $Al(CH_3CN)_6^{3+}$ (A, −34 ppm), $AlCl(CH_3CN)_5^{2+}$ (B, −24 ppm), and $AlCl_2(CH_3CN)_4^+$ (C, −14 ppm).

The Al NMR spectra of ternary solutions are quite similar in their appearance to those of binary solutions. They show that, when r increases, the intensity of the line coming from $AlCl_4^-$ (102 ppm) increases whereas the high-field signal observed at about −25 ppm tends to disappear and vanishes when the value $r = 1$ is reached.

The line at 102 ppm is very narrow (3 Hz) whatever the r value; we assume that neither the anion $Al_2Cl_7^-$ nor the neutral complex $AlCl_3{\cdot}CH_3CN$ is present at significant concentrations since, when formed, each of these species leads to a chemical exchange with $AlCl_4^-$ and the resulting NMR signal is very broad (~700 Hz).[14] No signal can be detected in the ^{35}Cl NMR spectra of ternary solutions for any r value. We conclude that most Cl atoms are bonded to aluminum. Then the only significant anion is $AlCl_4^-$. All other possible negative species have concentrations below 1%.

The measurement of the low- and high-field waves obtained after integration yields for each solution the relative concentrations of the anion $AlCl_4^-$ and of the penta- and hexacoordinated aluminum species measured all together. The variation of the ratio $q' = [AlCl_4^-]/([Al^V] + [Al^{VI}])$ is shown in Figure 1 for $r \leq 0.7$. The balance between ionic charges may be written as

$$[AlCl_4^-] = \bar{q}\,\{[Al^V] + [Al^{VI}]\} + [N(CH_3)_4^+]$$

if $\bar{q}$ stands for the previously defined "weighed average cationic charge".[2,10]

The introduction of r and q' expressions in the above relation yields directly the "measured average charge" $\bar{q}$ (Figure 1): $\bar{q} = q'(1 - r) - r$.

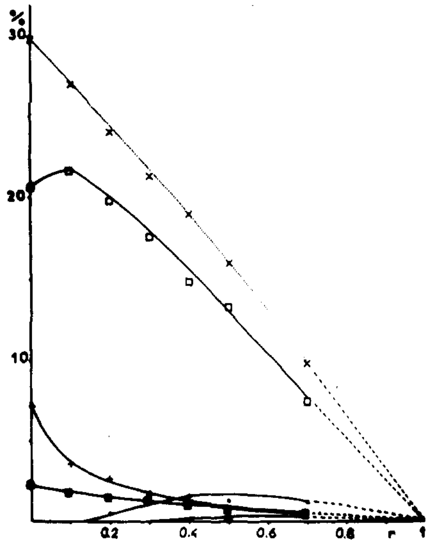

Figure 2. $AlCl_3/CH_3CN/N(CH_3)_4Cl$ system. Plot of the high-field Al NMR spectra vs. r: ×, total population of high field species; ■, □, ●, +, and ▲ stand for A, B, C, D, and E species, respectively.

According to the method previously described,[2,10] we have performed a curve analysis of the high-field signal in order to know the relative concentrations of Al^V and Al^{VI} species (Table I, Figure 2) and to calculate the value of $\bar{q}$ for each r value (Figure 1).[16]

When r increases, the fitting becomes unsatisfactory if based only on the previously known four bands A, B, C, and D, and the presence of a new broad band (E) located at −6.3 ppm has to be taken into account. We assign then the first four bands A, B, C, and D to the previously identified species. The last band, E, must correspond to the neutral octahedral complex $AlCl_3{\cdot}3CH_3CN$ since q_E was found equal to 0 (Figure 1) and the only other possible species $AlCl_3{\cdot}2CH_3CN$ should be expected in the +50 ppm range.[17] The chemical shift of E, −6.3 ppm, is very close to the value that we may estimate for each isomer of such a complex from the previously calculated pair-wise interaction parameters.[2] This assignment is consistent with the interpretation suggested by other authors in a recent note.[13] The stereoisomerism of the $AlCl_3(CH_3CN)_3$ complex may be deduced by using the semiempirical model for quadrupolar relaxation derived by Valiyev[18] from point-charge interactions. This complex may adopt two configurations: the so-called *mer* and *fac* ones.[19] According to the Valiyev model, the *fac* isomer (C_{3v}) should lead to a narrow NMR line whereas the *mer* isomer (C_{2v}) must correspond to a broad signal. Since the observed signal is very broad (~1400 Hz), it indicates the formation of the *mer* form of the neutral complex $AlCl_3(CH_3CN)_3$.

---

(11) The cation $N(CH_3)_4^+$ was chosen because previous results obtained in the laboratory[12] had shown that interactions of CH_3CN with this cation are much weaker than those with Li^+ or Na^+, which are generally used in this type of experiments.[3,13] r values greater than 1 are not possible since, in this case, tetramethylammonium chloride is not dissolved completely.

(12) J. P. Roche, Thesis, Bordeaux, 1971.

(13) F. W. Wehrli and R. Hoerdt, *J. Magn. Reson.*, **42**, 334 (1981).

(14) See ref 15 ($Al_2Cl_7^-$) and data in paragraph III ($AlCl_3/CH_3CN$) of Results and Discussion.

(15) U. Anders and J. A. Plambeck, *J. Inorg. Nucl. Chem.*, **40**, 38 (1978).

(16) Since the spectra were recorded at 23.45 MHz instead of 65.14 MHz, we have checked, for the solution corresponding to $r = 0$, that the deconvolution was feasible by using the peak parameters (position and width) of the four bands A, B, C, and D determined at 65.14 MHz.[2] The computer program was allowed to adjust only the heights of the four known peaks. The fitting of experimental and calculated spectra was satisfactory, and the concentrations found were quite consistent with those obtained after analysis of the spectra recorded at 65.14 MHz.

(17) J. Derouault, P. Granger, and M. T. Forel, *Inorg. Chem.*, **16**, 3214 (1977).

(18) K. A. Valiyev and M. H. Zripov, *Zh. Strukt. Khim.*, **7**, 494 (1966).

(19) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders, Philadelphia, 1977.

(20) M. F. Brown, B. R. Cook, and T. E. Sloan, *Inorg. Chem.*, **14**, 1273 (1975).

(21) The curve analysis shows that the apparent area of the D_0 signal for the dilute solution is too high if compared with that found in binary mixtures ($R = 37.4$).[2] We assume that this peak is superimposed upon that observed at −10 ppm for the concentrated solution, and a calculation based upon the balance of ionic charges leads to the relative proportion reported in Table II.

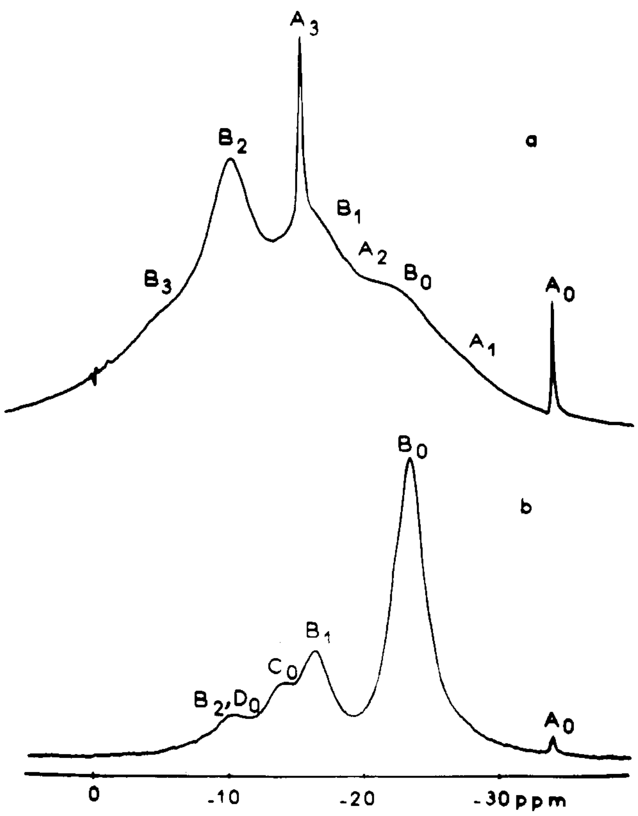

Figure 3. High-field part of the Al NMR spectra of the mixtures $AlCl_3/CH_3CN/H_2O$: (a) $R = 6.3, S = 0.4$; (b) $R = 98, S \approx 0.01$.

The variations of concentrations may be explained by the reactions

$$Al(CH_3CN)_5^{3+} + Cl^- \rightleftarrows AlCl(CH_3CN)_5^{2+}$$

$$Al(CH_3CN)_6^{3+} + Cl^- \rightleftarrows AlCl(CH_3CN)_5^{2+} + CH_3CN$$

$$AlCl(CH_3CN)_5^{2+} + Cl^- \rightleftarrows AlCl_2(CH_3CN)_4^{+} + CH_3CN$$

$$AlCl_2(CH_3CN)_4^{+} + Cl^- \rightleftarrows AlCl_3(CH_3CN)_3 + CH_3CN$$

$$AlCl_3(CH_3CN)_3 + Cl^- \rightleftarrows AlCl_4^- + 3CH_3CN$$

According to these reactions, the increase of the r values must lead to the formation of the most chlorinated species. Table I shows that this relation is corroborated satisfactorily. We observe furthermore (Figure 2) that the relative concentrations of Al^{V} and Al^{VI} species, although varying, are not drastically modified when r increases. The $AlCl(CH_3CN)_5^{2+}$ complex is always the most important component, and populations of $AlCl_2(CH_3CN)_4^+$ and $AlCl_3(CH_3CN)_3$ remain low. This fact suggests that the tendency for the occurrence of the reaction (with $q > 0$)

$$AlCl_{3-q}(CH_3CN)_{3+q}{}^{q+} + Cl^- \rightarrow AlCl_{4-q}(CH_3CN)_{2+q}{}^{(q-1)+} + CH_3CN$$

increases when the number of bonded Cl atoms increases.

II. $AlCl_3/CH_3CN/H_2O$ Mixtures. The influence of H_2O upon the $AlCl_3/CH_3CN$ system may be described with the analysis of two typical solutions: a concentrated one ($R = [CH_3CN]/[AlCl_3] = 6.3$ and $S = [H_2O]/[AlCl_3] = 0.4$) and a dilute one ($R = 98$, $S \simeq 0.01$).

The Al NMR spectra have been recorded at 65.14 MHz; they display the characteristic narrow line at +102 ppm due to $AlCl_4^-$ and a high-field signal with several components which are modified when the S ratio is changed (Figure 3). Besides the four previously known bands A, B, C, and D,[2] additional peaks are observed: a narrow line at −15.4 ppm, two broad bands at −16.5 and −10 ppm, and two minor features at ca. −28 and ca. −5 ppm. They must be assigned to partly hydrated cations. With the previously known data for the A, B, C, and D species, the curve analysis of both spectra yields the peak parameters of all other detected signals. Furthermore, there is evidence for the presence of a broad feature at −21.6 ppm (Table II).

Table II. Al NMR Data Related to the $AlCl_3/CH_3CN/H_2O$ Mixtures[a]

	shift,[g] ppm		$R = 6.3$, $S = 0.4$		$R = 98$, $S = 0.01$	
	calcd[b]	obsd	$\Delta\nu_{1/2}$, Hz	%	$\Delta\nu_{1/2}$, Hz	%
A_0	−33.96	−34	12	0.4	20	0.5
A_1	−27.24	−27.4	~900	11		
A_2 trans	−20.52	−21.6	380	6.4		
cis	−21.05					
A_3 *mer*	−14.86					
fac	−15.40	−15.40	23	1.6		
A_4 trans	−9.20					
cis	−9.73					
A_5	−4.6					
A_6	0	0[c]				
B_0	−23.96	−24	380	7.7	165	63
B_1 23[d]	−17.24	−16.5	380			
33	−16.53					
B_2 33	−9.63	−10.1	320	22.5	200	3.5[e]
32	−9.10					
23	−10.34					
B_3 23	−3.97	−4.7	900	23		
22	−3.44					
33	−2.73					
B_4 32	+1.92					
23	+1.71					
B_5	+8.24					
C_0 trans	−13.96	−14			200	15
D_0		−11.9[f]	810	8.7	200	4.5[e]

[a] $A_x = Al(H_2O)_x\,(CH_3CN)_{6-x}{}^{3+}$; $B_x = AlCl(H_2O)_x(CH_3CN_{5-x}{}^{2+}$. [b] Calculations done according to the pair-wise interactions model.[16] [c] This line observed only in aqueous solution of $AlCl_3$ is the Al NMR chemical shift reference. [d] Configuration number according to the stereochemical notation used on coordination chemistry.[20] [e] See ref 21. [f] This line shifts from −11.9 to −10 ppm. [g] Shift increments: NN, −2.83 ppm; NO, −1.15 ppm; OO, 0 ppm; ClO, 2.06 ppm; NCl, −0.33 ppm.

According to the Valiyev model,[18] the only partly hydrated cation which may give rise to a narrow Al NMR line is the *fac* form of the $Al(H_2O)_3(CH_3CN)_3^{3+}$ cation. Consequently, we assign the line at −15.4 ppm to this species. It is then possible to calculate the chemical shift for each cation in the series $[Al(H_2O)_x(CH_3CN)_{6-x}]^{3+}$[22] (Table II). These cations will be written thereafter as A_x. The bands at −28 and −21.6 ppm must be assigned then to A_1 and A_2 species, respectively. With regard to the peak at −16.5 ppm, it is questionable whether it must be assigned to the *mer*-A_3 cation or to a B_x cation. The ionic charge q of the corresponding species may be estimated from the curve analysis data (Table II). Within the experimental errors, we have found $q = 2$. We discard then the *mer*-A_3 hypothesis, and we assign the band at −16.5 ppm to a cation B_x: $AlCl(H_2O)_x(CH_3CN)_{5-x}^{2+}$. Since no signal can be detected between the bands due to B_0 (−24 ppm) and this B_x species (−16.5 ppm), the latter must be assigned to the B_1 cation.[23] The chemical shift of all B_x species may be calculated by using the pairwise interactions model (Table

---

(22) E. R. Malinowski, *J. Am. Chem. Soc.*, **91**, 4701 (1969).

(23) This assignment implies that the order of magnitude of the equilibrium constant of the reaction $B_x + H_2O \rightleftarrows B_{x+1} + CH_3CN$ does not depend upon the x value, according to the results obtained for analogous mixtures.[9]

Table III. Infrared and Raman Data Related to the AlX_3/CH_3NO_2 Mixtures

$AlCl_3/CH_3NO_2$				$AlBr_3/CH_3NO_2$				
solid		soln		solid		soln		
IR	R	IR	R	IR	R	IR	R	assignt
598 m				596 m				$w(NO_2)$
	546 w			546 m				$r(NO_2)^a$
538 s, br	532 w	547 vs, br	~540 w	444 s, br		450 s, br	~450 w	$\nu_d(AlX_3)$
		497 s, br	~490 w			405 s, br		$\nu_d(AlX_4^-)$
			480 m			480 s	478 s	$\pi(NO_2$ (free))
410 s	406 s	408 s	408 s, p	372 m	372 w	370 sh	368 w, p	$\nu(AlO)^a$
		379 m						$\nu(AlO_6)^b$
			350 s, p				211 s, p	$\nu_s(AlX_4^-)$
328 m	324 s	318 w	323 s, p	234 m	233 s	234 w	236 w, p	$\nu_s(AlX_3)^a$
			290 w, p				290 w, p	$\nu_s(AlO_6)^b$
214 m	220 m		214 w	186 m				$\delta(AlON)$, $\tau(NO)$
187 m	190 m			166 m	161 m			
			182 w				113 w	$\delta_d(AlX_4^-)$
164 s	165 m		162 w, p	124 m	124 m		125 w, p	$\delta_s(AlX_3)$
	138 m			99 m	97 m			$r(AlX_3)$
	103 sh							
	74 s			73 s				

[a] Approximate assignments for normal modes which involve probably several vibration groups. [b] See the NMR analysis. Key: s, strong; m, medium; w, weak; sh, shoulder; br, broad; p, polarized.

II). The results lead to assign the bands at −10 and −4.7 ppm observed at high concentration to the B_2 and B_3 cations, respectively.

If we now consider the concentrations of A_x species in the concentrated solution, we note that the sum of the percentage of the A_x species reaches 18% when $S = 0.4$ (Table II) and is then greater than the abundance of A_0 when $S = 0$ (5%, see Table I). Since we observe simultaneously that (i) the concentration of D_0 decreases quickly and (ii) the sum $\{[A_x] + [D_0]\}$ is a constant, we conclude that the contribution of the following reaction is very important:

$$Al(CH_3CN)_5^{3+} + H_2O \rightleftarrows AlH_2O(CH_3CN)_5^{3+}$$

We note also that the sum of the concentrations of B_x species is constant too. These results indicate that, beside the above reaction of addition only the following substitutions take place:

$$A_x + H_2O \rightleftarrows A_{x+1} + CH_3CN$$

$$B_x + H_2O \rightleftarrows B_{x+1} + CH_3CN$$

Under our experimental conditions, we have characterized the steps involving $x = 0$–2 for A_x as well as for B_x species.

These results are consistent with the interpretation proposed by Ruben and Reuben[9] in their proton magnetic resonance analysis of the $Al(ClO_4)_3/H_2O/CH_3CN$ system. Furthermore, the concentrations of the D_0, A_x, and B_x species that we have found account for the fact that the average ionic charge $\bar{q}$ is not modified upon addition of H_2O (Table II); this observation is consistent with the results obtained from conductivity measurements,[24] which had shown that the conductivity, and thus the number and the charges of the ions, are not severely altered upon H_2O addition.

III. $AlCl_3/CH_3CN/CH_3NO_2$ Mixtures. The studied solutions of $AlCl_3$ in mixtures of CH_3CN/CH_3NO_2 were prepared in such a way that the ratio $([CH_3CN] + [CH_3NO_2]/[AlCl_3])$ was kept equal to 7.3. The composition of each solution will be referred to by the ratio $p = [CH_3CN]/[CH_3NO_2]$.

It is necessary to investigate first the particular interaction between $AlCl_3$ and CH_3NO_2 by means of Al NMR and vibrational spectroscopy. For this purpose, we have prepared the 1:1 solid adducts $AlCl_3{\cdot}CH_3NO_2$ and $AlBr_3{\cdot}CH_3NO_2$.

(1) Vibrational Analysis of the 1:1 $AlX_3{\cdot}CH_3NO_2$ Adducts. The infrared and Raman spectra have been recorded between 50 and 4000 cm^{-1}; our infrared data for $AlCl_3{\cdot}CH_3NO_2$ are consistent with previous results.[25]

Table IV. Al NMR Data Related to the $AlCl_3/CH_3CN/CH_3NO_2$ Mixtures[a]

A'_x	calcd,[d] ppm	obsd, ppm	B'_x	calcd, ppm	obsd, ppm
A	−33.96	−34	B_0	−23.96	−24
A'_1	−29.84		B'_1 23[b]	−19.84	−19
			33	−18.91	
A'_2 trans	−25.72	−28			
cis	−26.03		B'_2 33	−14.17	
			32	−13.86	
A'_3 *mer*	−22.22		23	−15.10	
fac	−22.53	−22.5			
			B'_3 23	−10.67	
A'_4 *trans*	−18.72		22	−10.36	
cis	−19.03		33	−9.43	
A'_5	−15.84		B'_4 32	−5	
			23	−6.24	
A'_6	−12.96	−13[a]			
			B'_5	−2.12	

[a] $A'_x = Al(CH_3NO_2)_x(CH_3CN)_{6-x}{}^{3+}$; $B'_x = AlCl(CH_3NO_2)_x(CH_3CN)_{5-x}{}^{2+}$. [b] This line is observed only in solution of $AlCl_3$ in CH_3NO_2. [c] Configuration number according to the stereochemical notation used in coordination chemistry.[20] [d] Shift increments: NN, −2.83 ppm; NO, −1.80 ppm; OO, −1.08 ppm; ClO, +1.63 ppm; NC, −0.33 ppm.

Spectra above 600 cm^{-1} denote the complexation of CH_3NO_2 but do not allow the discussion of the structure of the adducts. Data below 600 cm^{-1} are reported in Table III, and comparison with the spectra of previously known analogous compounds such as $AlX_3{\cdot}(CH_3)_2O$,[26] $AlX_3{\cdot}C_4H_8O$,[27] $AlX_3{\cdot}C_5H_5N$,[28] and $AlX_3{\cdot}(CH_3)_3N$[28] gives evidence that the adducts $AlX_3{\cdot}CH_3NO_2$ have a molecular structure involving a quasiregular tetrahedral framework.

The vibrational pattern of this series of compounds is quite simple and is well understood; thus the assignment of the main vibrational modes of the $OAlX_3$ framework of $AlX_3{\cdot}CH_3NO_2$ adducts is unambiguous and is reported in Table III.

(2) Vibrational and NMR Analysis of AlX_3/CH_3NO_2 Mixtures. The infrared and Raman frequencies of solutions

---

(24) G. Lancelin, B. Dubois, and B. Vandorpe, *Bull. Soc. Chim. Fr.*, **1**, 14 (1979).

(25) D. E. H. Jones and J. L. Wood, *J. Chem. Soc. A*, 1448 (1966).

(26) J. Derouault and M. T. Forel, *Ann. Chim.* (*Paris*), **6**, 131 (1971).

(27) J. Derouault and M. T. Forel, *Inorg. Chem.*, **16**, 3207 (1977).

(28) I. R. Beatie and G. A. Ozin, *J. Chem. Soc. A*, 2373 (1968).

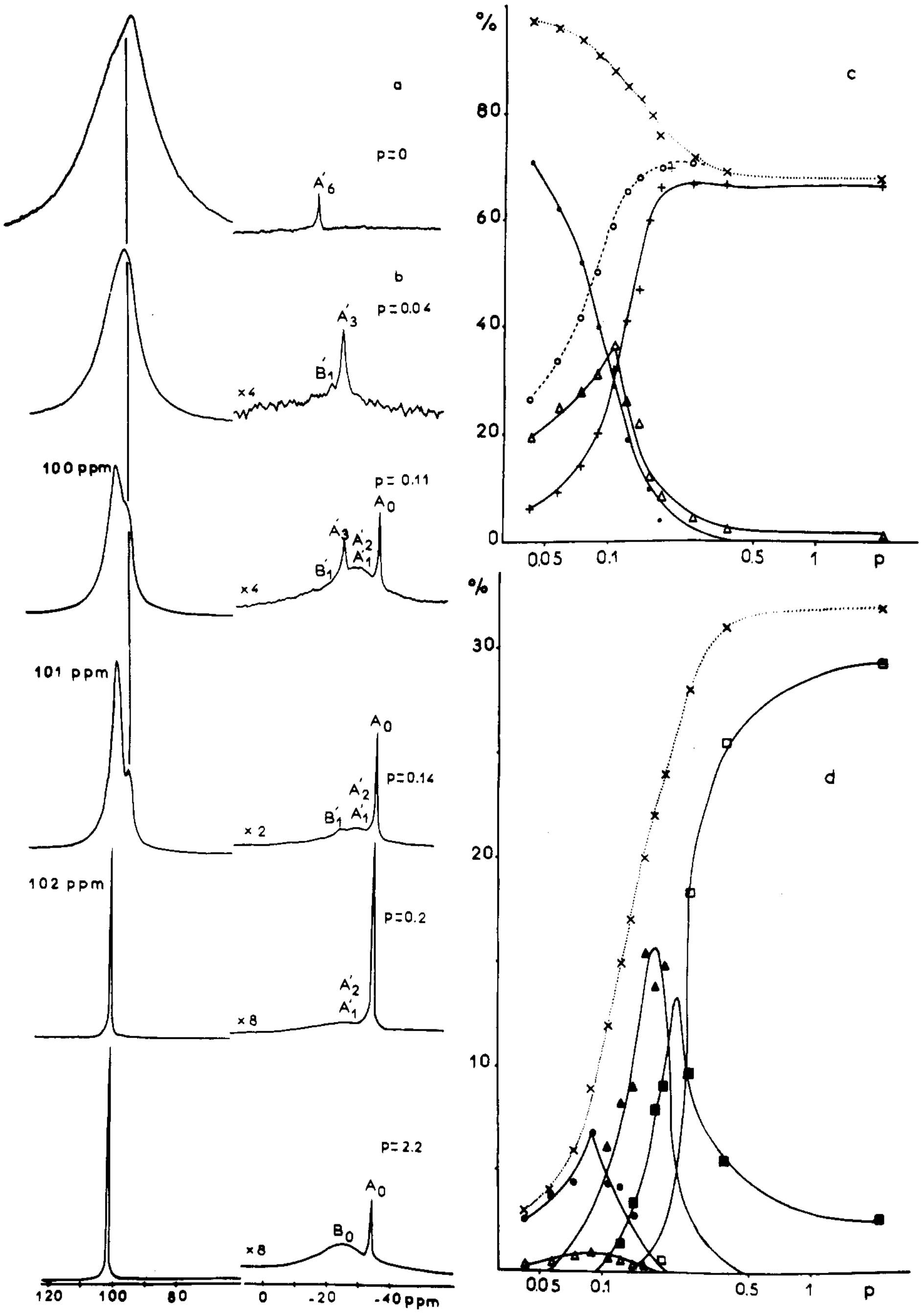

Figure 4. Al NMR spectra of the $AlCl_3/CH_3CN/CH_3NO_2$ mixtures. (a) $AlCl_3$ in pure CH_3NO_2. (b) $AlCl_3$ in CH_3CN/CH_3NO_2 mixtures, with five p values. (c) Curve analysis of tetrahedral species: ×, total percentage; ●, $AlCl_3 - CH_3NO_2$ (+97 ppm); ○, ($AlCl_4^-$ + $AlCl_3 - CH_3CN$) together (∼+100 ppm); +, $AlCl_4^-$ (+102 ppm); △, $AlCl_3 - CH_3CN$. (d) Curve analysis of octahedral species: ×, total percentage; ●, B'_1 (−19 ppm); △, A'_3 (−22.5 ppm); ▲, $A'_2 + A'_1$ (∼−28 ppm); ■, A_0 (−34 ppm); □, B_0 (−24 ppm).

of $AlCl_3$ and of $AlBr_3$ in CH_3NO_2 are listed in Table III; a number of bands are common with the spectra of the isolated solid 1:1 compounds. The existence in solution of the molecular 1:1 adducts is then established. Some additional bands arise in the infrared as well as in the Raman spectra and allow the unambiguous identification of the anions $AlCl_4^-$ and $AlBr_4^-$ from their characteristic frequencies.[29] The remaining unassigned two bands, located at 379 and 290 cm^{-1}, are ascribed to stretching modes of the counterion.

The Al NMR spectrum of the solution of $AlCl_3$ in CH_3NO_2 shows a very broad band ($\Delta\nu_{1/2}$ = 700 Hz) at +96 ppm (Figure 4a). Second, a weak narrow line ($\Delta\nu_{1/2}$ = 20 Hz) is observed at −13 ppm. These results agree with those of the literature only for the signal at +96 ppm.[30] Nevertheless, they are quite consistent with the above vibrational data, and the assignment is straightforward: the strongest band at +96 ppm is due to the molecular species $AlCl_3 \cdot CH_3NO_2$; this chemical shift may be compared with those of other known 1:1 adducts.[2,17] The signal close to +100 ppm corresponds to the $AlCl_4^-$ anion and the narrow line at −13 ppm should arise from the cation; as previously discussed[2] such a line width implies a regular tetrahedral or octahedral environment of the Al atom and then the negative value for the chemical shift leads to the conclusion that we are dealing with the $Al(CH_3NO_2)_6^{3+}$ cation.

(3) NMR Analysis of $AlCl_3/CH_3CN/CH_3NO_2$ Mixtures. The Al NMR spectra of 13 ternary solutions with p values

---

[29] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley-Interscience, New York, 1977.

[30] R. G. Kidd and D. R. Truax, *Can. Spectrosc.*, **14**, 1 (1969).

included in the range of 0–2.2 have been recorded at 23.45 MHz and five of them are reported in Figure 4b. They are deeply altered when p is modified: some narrow lines are observed, superimposed over large signals of which the positions and the width are sensitive to relative concentrations. We have performed the computer curve analysis of these spectra in order to determine the number, the position (Table IV), and the relative area of each component (Figure 4c,d).

Previous results[2] allow the assignment of the lines at +102, +97, −24, and −34 ppm to $AlCl_4^-$ $AlCl_3 \cdot CH_3NO_2$, $AlCl(CH_3CN)_5^{2+}$, and $Al(CH_3CN)_6^{3+}$, respectively. Among the still unassigned lines in the high-field part of the spectra, the narrow one at −22.5 ppm must be ascribed to the *fac* isomer of $[Al(CH_3NO_2)_3(CH_3CN)_3]^{3+}$ (A'_3)[31] according to the Valiyev model.[18] It is then possible to calculate the chemical shifts of each A'_x cation (Table IV) by using the pairwise interactions model.[22] The species A'_1 and A'_2 are calculated at −30 and −26 ppm, respectively, and are expected to give rise to very broad NMR bands.[18] We assign the broad band observed near −28 ppm to the resulting signal due to both species.

The last unassigned broad band, located at −19 ppm, could correspond either to the A'_4 or the B'_1 cations, according to calculated chemical shifts. We reject the A'_4 assignment because this band is observed in the same range of relative concentrations p as the A'_3 species (Figure 4d).

We note that the species $Al(CH_3CN)_5^{3+}$ has not been detected in any ternary mixtures with CH_3NO_2.

With regard to the low-field part of the spectra (Figure 4b), the shift of one of the two signals clearly demonstrates the occurrence of chemical exchange between $AlCl_4^-$ and an additional complex Y, which is not $AlCl_3 \cdot CH_3NO_2$. The nature of Y may be deduced from an estimate of the number of Al atoms and of CH_3CN involved in it. The number of Al atoms may be written as

$$[Al]_Y = 100 - [AlCl_3 \cdot CH_3NO_2] - 4\sum_x [A'_x] - 3\sum_x [B'_x]$$

in which $\sum_x [A'_x]$ and $\sum_x [B'_x]$ stand for the sum of percentages of A'_x and B'_x cations, respectively. On the other hand, we have recorded the proton magnetic resonance spectra of the studied solutions at various temperatures (Figure 5); their interpretation is not easy but they give evidence that no free CH_3CN molecules exist for p values lower than 0.26, even involved in exchange processes. Under these conditions, the number of CH_3CN bound in species Y may be written

$$[CH_3CN]_Y = 730\frac{p}{1+p} - \sum_x (6-x)[A'_x] - \sum_x (5-x)[B'_x]$$

Using the data reported in Figure 4c, we have found that the ratio $[Al]_Y/[CH_3CN]_Y$ remains equal to 1, within the experimental errors. This result leads to the formula of the Y species ($AlCl_3 \cdot CH_3CN \cdot nCH_3NO_2$) with n = 0, 1, or 2. It is then possible to estimate the chemical shift of Y by using the equations relative to an exchange between two unequally populated sites;[32] we have found $\delta(Y) = +95 \pm 2$ ppm. This value is very close to the chemical shift previously found for $AlCl_3 \cdot CH_3CN$ (+96 ppm);[2] we consequently conclude that the species Y is the molecular complex $AlCl_3 \cdot CH_3CN$.

The set of reactions which occur in the investigated mixtures is

$$4AlCl_3 \cdot CH_3NO_2 + 2CH_3NO_2 \rightleftarrows 3AlCl_4^- + Al(CH_3NO_2)_6^{3+}$$

$$AlCl_4^- + CH_3CN \rightleftarrows AlCl_3 \cdot CH_3CN + Cl^-$$

$$Al(CH_3NO_2)_2(CH_3CN)_4^{3+} + Cl^- \rightleftarrows AlCl(CH_3NO_2)(CH_3CN)_4^{2+} + CH_3NO_2$$

$$3Al(CH_3CN)_6^{3+} + AlCl_4^- + 2CH_3CN \rightleftarrows 4AlCl(CH_3CN)_5^{2+}$$

$$A'_x + CH_3CN \rightleftarrows A'_{x-1} + CH_3NO_2 \quad x = 1, 2, \text{ or } 3$$

Conclusion

We have applied to ternary solutions the method of investigation which was derived for the study of binary solutions of aluminum halides. When two Lewis bases are allowed to compete for complex formation with aluminum chloride, the base with the greater donor number tends to substitute the other one, but numerous intermediate mixed complexes exist in the mixtures. These intermediate species have been characterized and identified by using systematically the Malinowski and Valiyev models in order to estimate the position and the width of the Al NMR signal corresponding to each species.

Acknowledgment. We are indebted to Professor Lascombe for helpful discussions, to Mrs Chapelle for recording the NMR spectra, and to Dr. Brevard of Bruker, France, for the high-field NMR spectra.

Registry No. A_0, 25159-95-9; A_1, 60892-39-9; A_1', 80765-19-1; *trans*-A_2, 60895-30-9; *cis*-A_2, 60869-05-8; *trans*-A_2', 80765-20-4; *cis*-A_2', 80795-39-7; *mer*-A_3, 60895-31-0; *fac*-A_3, 60869-07-0; *mer*-A_3', 80765-21-5; *fac*-A_3', 80795-40-0; *trans*-A_4, 60895-34-3; *cis*-A_4, 60869-09-2; *trans*-A_4', 80765-22-6; *cis*-A_4', 80795-41-1; A_5, 60869-11-6; A_5', 80765-23-7; A_6', 80765-24-8; B_0, 60475-07-2; 23-B_1, 80765-25-9; 33-B_1, 80795-42-2; 23-B_1', 80765-26-0; 33-B_1', 80795-43-3; 33-B_2, 80765-27-1; 32-B_2, 80795-44-4; 23-B_2, 80795-45-5; 33-B_2', 80765-28-2; 32-B_2', 80795-46-6; 23-B_2', 80796-72-1; 23-B_3, 80765-29-3; 22-B_3, 80795-47-7; 33-B_3, 80795-48-8; 23-B_3', 80765-30-6; 22-B_3', 80795-49-9; 33-B_3', 80795-50-2; 32-B_4, 80765-31-7; 23-B_4, 80795-51-3; 32-B_4', 80765-32-8; 23-B_4', 80795-52-4; B_5, 80765-33-9; B_5', 80765-34-0; *trans*-C_0, 77123-00-3; D_0, 80063-19-0; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; $N(CH_3)_4Cl$, 75-57-0.

Supplementary Material Available: Table I (curve analysis of Al, NMR spectra of $AlCl_3$, CH_3CN, $ClN(CH_3)_4$ solutions) and Figure 5 (^1H NMR spectra of $AlCl_3/CH_3CN/CH_3NO_2$ mixtures) (2 pages). Ordering information is given on any current masthead page.

---

(31) Mixed cations with CH_3NO_2 will be referred thereafter by the notation A'_x and B'_x, similar to that used for the mixed hydrates.

(32) M. L. Martin, J. J. Delpuech, and G. J. Martin, "Practical NMR Spectroscopy", Heyden: London, 1980.