Contribution from the Laboratoire de Spectroscopie Infrarouge,
Université de Bordeaux I, 33405, Talence, France, and the Laboratoire de Chimie Théorique,
Université de Nancy I, Nancy, France

Spectroscopic Investigation of Aluminum Trihalide–Tetrahydrofuran Complexes. 2. Solutions of Aluminum Chloride or Bromide in Tetrahydrofuran and in Tetrahydrofuran–Dichloromethane[1]

J. DEROUAULT,*[2a] P. GRANGER,[2b] and M. T. FOREL[2a]

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The $AlCl_3$–THF system has been extensively investigated by infrared, Raman, and ^{27}Al NMR spectroscopy in the range of the molar ratio of [THF]/[$AlCl_3$] of 1–250. At room temperature the system consists mainly of the molecular species $AlCl_3$·THF and $AlCl_3$·2THF, the latter giving rise to cis–trans isomerism. We also found that $AlCl_3$·2THF is slightly dissociated into $AlCl_4^-$ and $[AlCl_2(THF)_4]^+$. We analyzed the concentration and temperature dependence of the equilibria and estimated equilibrium constants and activation energies. Analogous results were obtained for the $AlBr_3$–THF system but for the ionic dissociation.

Introduction

Tetrahydrofuran (THF) is a frequently used solvent for organometallic or coordination compounds. This ether acts as a strong Lewis base and is able to stabilize a number of unstable species.

On the other hand, aluminum trihalides are used for their catalytic properties, or constitute a component in $AlCl_3$–WCl_6-type catalysts. Furthermore, aluminum trihalides are formed easily through dismutation processes in reactions which employ the important alkyl halide–aluminum compounds.[3,4]

Although a complete analysis of the specific interactions of aluminum trihalides with THF should therefore provide valuable and useful information, only a few papers have, as yet, been published. For instance, from conductivity measurements, Evans et al.[5] were led to propose that the THF ring opens upon $AlCl_3$ attack. Other conductivity results[6,7] were interpreted by the ionic dissociation equilibrium

$$2Al_nCl_{3n} \rightleftarrows Al_nCl_{3n+1}^- + Al_nCl_{3n-1}^+ \qquad (1)$$

On the basis of our infrared spectra,[8,9] we suggested the occurrence of the simultaneous equilibra between molecular species (eq 2 and 3). We proposed also that the THF ring

$${}^1/_2 Al_2Cl_6 + THF \rightleftarrows AlCl_3 \cdot THF \qquad (2)$$

$$AlCl_3 \cdot THF + THF \rightleftarrows AlCl_3 \cdot 2THF \qquad (3)$$

stays closed under anhydrous $AlCl_3$ attack and that only coordination compounds, as shown by equilibra 2 and 3, are formed.

O'Reilly[10] and Haraguchi et al.[11] have investigated solutions of $AlCl_3$ or $AlBr_3$ in THF by ^{27}Al NMR and concluded that Al_2Cl_6 or Al_2Br_6 are the dissolved species, rather than coordination compounds. This interpretation does not, however, agree with related infrared data.[7,8]

The discrepancies between the above conclusions convinced us that a new study of the $AlCl_3$–THF system was necessary. This study is facilitated by our recent results on related solid compounds.[12]

In this paper, we present and discuss new experimental infrared, Raman, and ^{27}Al NMR spectroscopic data on the AlX_3–THF systems (X = Cl,Br). A large part of our work was done with the $AlCl_3$·THF (or $AlBr_3$·THF) 1:1 complex in THF solutions, but because of saturation effects in pure THF at $AlCl_3$ concentrations below the maximum we wished to investigate, we required a second inert solvent to keep complex species in solution. This solvent must dissolve appreciable amounts of the AlX_3·THF 1:1 adduct and not displace the bound THF. It must have only weak infrared bands in the 250–600-cm^{-1} range and, if possible, permit the examination of some characteristic bands of bound THF. We found that dichloromethane satisfied these conditions best.

Experimental Section

Preparation of Solutions. Dichloromethane (Prolabo spectrograde) was fractionally distilled and stored over molecular sieves (size 4 Å). Just before use, it was passed onto P_2O_5, and distilled, in vacuo, directly into the vessel used to prepare the solutions. THF (Merck spectrograde) was passed onto P_2O_5 and distilled, in vacuo, directly into the vessel. The 1:1 AlX_3·THF (X = Cl, Br) complexes were prepared as previously described.[12]

A stock solution (c = 0.03 M) of the 1:1 solid $AlCl_3$·THF (or $AlBr_3$·THF) in CH_2Cl_2 was prepared first on a vacuum line. Increasing dilutions with THF were prepared in a drybox by mixing equal aliquots of the stock solution and THF–CH_2Cl_2 solutions of such proportions that the molar ratio x = [THF]/[AlX_3] varied between 1 and 250. Under these conditions, the AlX_3 concentration in the total mixture is kept constant at $c/2$. The molar ratio x was kept ≥ 1; since the interaction between AlX_3 and CH_2Cl_2 is weaker than that between AlX_3 and THF, we found that, under the above condition, the interaction between AlX_3 and CH_2Cl_2 was negligible.

Spectra. The infrared spectra were recorded on a Perkin-Elmer 521, using the standard slit program. The cell was equiped either with KRS 5 or polyethylene windows. By this, we found that no halogen exchange occurred between the windows and the $AlCl_3$ solutions, but some difficulties arose in this respect with $AlBr_3$ solutions. The background spectrum of each solvent mixture was recorded under exactly the same conditions as for the corresponding solution and was subtracted in order to obtain the spectrum of the dissolved species only. The infrared cell was dismantled after each measurement and cleaned.

The Raman spectra were recorded on a Coderg with triple monochromator and conventional dc amplification using a 164 Spectra-Physics Ar$^+$ laser, adjusted at ca. 400 mW at 488 nm, as a light source. The resolution was about 2 cm^{-1}. The solutions were placed into a rotating cell in order to avoid decomposition under the laser beam. The wavelength calibration error for both vibrational spectrometers was less than 2 cm^{-1}.

Most of the ^{27}Al NMR spectra were recorded by the Bruker HX90 of Nancy University, using a ^{13}C insert at 22.63 MHz. The magnetic field had to be lowered in order to obtain the ^{27}Al resonance, and the measurements were performed with only flux stabilization. Consequently, chemical shifts were measured with an error of ±2 ppm. The external reference was a solution of $AlCl_3$ in H_2O. High concentration solutions were analyzed in the frequency-sweep mode, while the Fourier transform method was used for dilute solutions.

Some complementary measurements have been made on the new pulsed NMR spectrometer, Bruker WH90 (multinuclear series with a built-in frequency synthesizer), of the University of Rouen. The higher sensitivity of this apparatus and the use of the LOCK device permit one to confirm the existence of the weakest peaks, particularly in experiments on dilute solutions which need numerous scannings.

All sampling cells were filled in a drybox.

Results and Discussion

The quantity x is defined as the ratio of the number of THF molecules (*including* those bound to AlX_3 in the initial 1:1

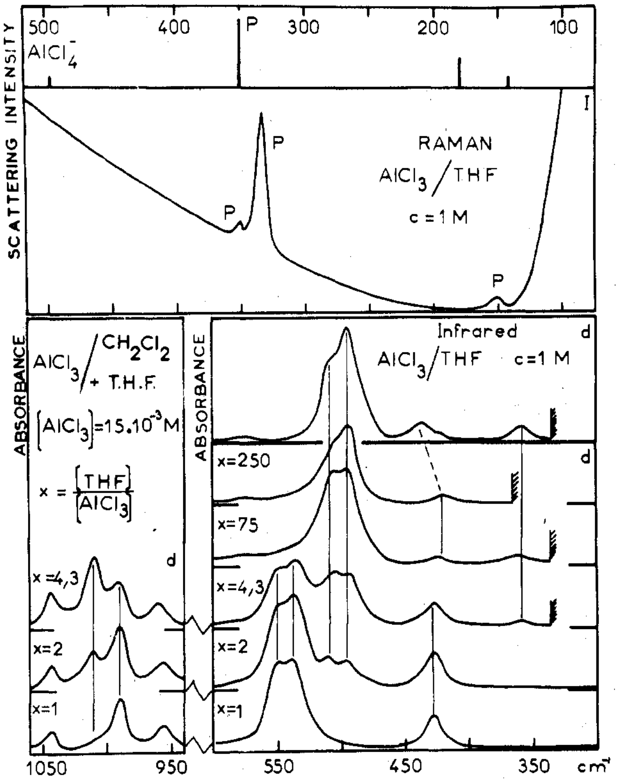

Figure 1. Vibrational spectra of $AlCl_3$ complex species in neat THF and in THF–CH_2Cl_2 mixtures. Positions of $AlCl_4^-$ Raman lines are shown for comparison. The broken line shows the limit of transparency of the solvent mixtures. Absolute values for the absorbances are given in Table II.

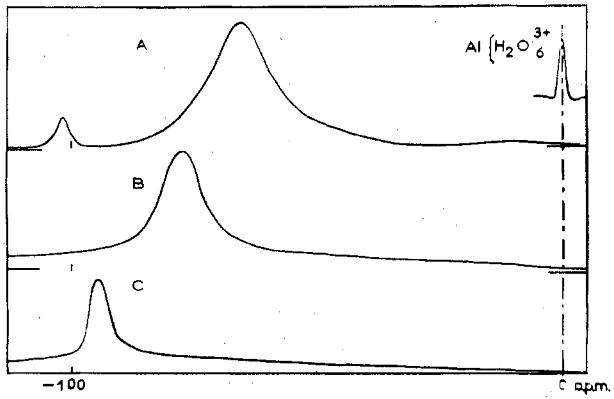

Figure 2. ^{27}Al NMR of $AlCl_3$ in mixed solvents (THF–CH_2Cl_2). (A) solution in neat THF, $c = 0.95$ M, frequency-sweep mode; (B and C) solutions in THF–CH_2Cl_2 mixtures, Fourier transform method; B: $c = 3 \times 10^{-2}$ M, x = [THF]/[$AlCl_3$] = 11, 2048 scans; C: $c = 3 \times 10^{-2}$ M, $x = 1$, 1024 scans.

Table I. Spectroscopic Characteristics of the Various Complex Species Identified in Solutions of $AlCl_3$ or $AlBr_3$ in THF[a]

$AlCl_3 \cdot THF$ (A)	ν(IR): 1043 (w), 991 (m), 953 (w), 865 (m), 844 (m), 546 (vs), 537 (vs), 430 (m) δ ^{27}Al NMR: −94 ppm (~120 Hz width)
cis-$AlCl_3 \cdot 2THF$ (B)	ν(IR): 1044 (w), 1012 (m), 964 (w), 854 (m), 510 (vs), 496 (vs), 415 (w) ν(Raman): 930, 860 (p), 329 (p), 150 (p) δ ^{27}Al NMR: −63 ppm (~500 Hz width)
trans-$AlCl_3 \cdot 2THF$ (D)	ν(IR): 490 (vs), 420 (m) δ ^{27}Al NMR: −63 ppm (~240 Hz width)
$AlCl_4^-$ (C)	ν(IR): 494 (vs) ν(Raman): 350 (p) δ ^{27}Al NMR: −102 ppm (6–180 Hz width)[b]
$Al(THF)_4Cl_2^+$ (C)	ν(IR): 440 (m), 360 (m) δ ^{27}Al NMR: −9 ppm (~250 Hz width)
$AlBr_3 \cdot THF$	ν(IR): 1044 (w), 990 (m), 960 (w), 860 (m), 840 (m), 440 (vs), 396 (m)
$AlBr_3 \cdot 2THF$	ν(IR): 1006 (m), 420 (vs) ν(Raman): 930, 860 (p), 206 (p) δ ^{27}Al NMR: −49 ppm (~500 Hz width)

[a] Infrared intensities: vs, very strong; s, strong; m, medium; w, weak. Raman: p, polarized. ν in cm⁻¹. [b] See text.

$AlX_3 \cdot THF$ complex) to the number of AlX_3 molecules.

Solutions of $AlCl_3$. $x = 1$. The infrared and NMR results for $x = 1$ are shown in Figures 1 and 2, respectively. Comparison with Figure 1 in paper 1[12] shows that the complex in solution has the same formula as the 1:1 solid compound, $AlCl_3 \cdot THF$ (see A in Table I). The infrared bands observed for the bound THF correspond well to the spectrum of the 1:1 adduct. The splitting of the strong band near 550 cm⁻¹ is caused by a removal of the degeneracy.[12] This could be observed because of the decrease of the band widths with respect to the solid compound. For the solid compound, the band at 439 cm⁻¹ was assigned to a mode involving essentially the Al–O stretch.[12] The corresponding absorption in solution is shifted towards low frequencies by about 10 cm⁻¹, as can be seen in Figure 1. This is, in fact, a typical result for such coordination bonds.[13]

A weak band is observed at the position of the strongest absorption of free THF (1064 cm⁻¹); it denotes a slight dissociation of the 1:1 adduct according to equilibrium 4.

$$\tfrac{1}{2}Al_2Cl_6 + THF \rightleftarrows AlCl_3 \cdot THF \qquad (4)$$

$x > 1$. With increasing values of x, the infrared spectra (Figure 1) give strong evidence for the formation of another compound (referred herein as B); for instance, there are new bands at 1012, 510, 496, and 415 cm⁻¹. On the other hand, the 1:1 adduct disappears. The comparison of these spectra with that of the 1:2 solid compound[12] shows that the new band near 1000 cm⁻¹ corresponds to bound THF. However, the bands in the low-frequency range of the solution and solid-state spectra are not identical, although similar. Furthermore, for the highest value of x (250), we see that the intense (split) band near 500 cm⁻¹ shows the existence of an additional third species (referred to as C).

The infrared spectrum of the 1 M solution of $AlCl_3$ in neat THF and the corresponding spectrum for $x = 250$ look quite similar. This suggests that the dissolved species may have the same composition in both media. If we now look at the Raman spectrum of the 1 M solution in neat THF (Figure 1), we notice that it exhibits one strong, polarized band at 330 cm⁻¹ and two weak, polarized bands at 350 and 150 cm⁻¹.

The ^{27}Al NMR spectra of the mixed solutions (x = 1, 11) and of a solution in neat THF are shown in Figure 2. We see that the change of the molar ratio [THF]/[$AlCl_3$] results in a shift of the main peak from −94 to −63 ppm, and causes the appearance of two weak peaks at −102 and −9 ppm for the solution in neat THF. Since the concentration ranges are the same in this NMR analysis and in the above vibrational study, we assign the two weak peaks to compound C.

Compound C is easily identified as an ionic complex since the infrared absorption at 495 cm⁻¹, the Raman line at 350 cm⁻¹, and the NMR peak at −102 ppm are the well-known typical features of $AlCl_4^-$.[12,14] This complex is likely to be identical with the 1:2 solid compound, the formula of which was demonstrated to be [$AlCl_4^- AlCl_2(THF)_4^+$].[12] Therefore, the weak broad NMR peak at ca. −9 ppm must be assigned to the octahedral $AlCl_2(THF)_4^+$ cation. The expected ratio of the areas of the bands at −102 and −9 ppm should be unity; we have found 1 ± 0.1. This view is also supported by the

Table II. Infrared Parameters of Equilibrium II

$x - 1$	d_{546}	d_{510}	$\log(d_{510}/d_{546})$ $m = 1$	$\log(d_{510}/(d_{546})^2)$ $m = 2$	$\log(d_{510}/d_{(546)}^3)$ $m = 3$
0.33	0.52 ± 0.01	0.04 ± 0.01	−1.12 ± 0.12	−0.85 ± 0.15	−0.55 ± 0.15
0.66	0.45 ± 0.01	0.07 ± 0.01	−0.81 ± 0.07	−0.46 ± 0.08	−0.11 ± 0.10
1	0.43 ± 0.01	0.10 ± 0.01	−0.63 ± 0.06	−0.27 ± 0.07	+0.10 ± 0.08
3.33	0.30 ± 0.01	0.24 ± 0.01	−0.09 ± 0.03	+0.42 ± 0.05	0.95 ± 0.06
10	0.15 ± 0.01	0.40 ± 0.01	+0.43 ± 0.04	1.25 ± 0.07	2.10 ± 0.08
74	0.02 ± 0.01	0.46 ± 0.01	1.35 ± 0.30	3.2 ± 0.5	4.8 ± 0.7

weak infrared bands in the range of 280–450 cm^{-1}, bands which are analogous to those of the 1:2 solid compound. This interpretation is to be compared to Waki's results[6,7] (see equilibrium 1), but we emphasize the fact that the ionic fraction represents only about 10% of the total dissolved complex species.

Compound B is characterized by its infrared, Raman, and NMR spectra (Table I). Its stoichiometry is obtained by analysis of the infrared spectra when x is increased. The formation equilibrium may be written

$$m\mathrm{AlCl_3} + nm\mathrm{THF} \rightleftarrows (\mathrm{AlCl_3}\cdot(n+1)\mathrm{THF})_m \qquad (5)$$

The parameter m accounts for the well-known ability of such complexes to aggregate. The equilibrium constant k_c is then

$$k_c = \frac{c_0 y}{[c_0(1 - my)]^m [c_0(x - 1 - nmy)]^{nm}} \qquad (6)$$

where c_0 is the analytical molar concentration of $AlCl_3$ and y the mole fraction of the new complex. The quantity x has the previous meaning. We assume the validity of Beer's law in our system since (a) the concentrations of the complexes are weak and (b) we limited our evaluation to the range x = 1.33–75; thus, only compound B contributes significantly to the infrared absorption at 510 cm^{-1}.

Therefore, we derive from eq 6 the linear equation (in terms of logarithms)

$$\log[d_{510}/(d_{546})^m] = nm \log(x - 1 - nmy) + \log[\epsilon_{510}/(\epsilon_{546})^m] + \log k_c + nm \log c_0 + \log l^{m-1} \qquad (7)$$

Here, d_{510}, ϵ_{510} and d_{546}, ϵ_{546} refer to the absorbance and to the molar absorptivity of the characteristic maxima of the compound B and of the 1:1 adduct, respectively, and l is the cell path. The reasonable assumption is made that nmy is negligible compared to $x - 1$; this means that the amount of newly fixed THF in compound B remains small with respect to the number of added moles of THF. This is certainly true for high x values; for the lowest x values, the relatively slow growth of the intensity of the bands of compound B with x justifies this assumption. We then plot the values of log $[d_{510}/(d_{546})^m]$ vs. log $(x - 1)$ for m = 1, 2, and 3 (see Table II) and reject all m except that which leads to a straight line: $m = 1$. The corresponding equation is thus

$$\log(d_{510}/d_{546}) = \log(x - 1) - 0.6 \qquad (8)$$

The formula of compound B is therefore ($AlCl_3$·2THF) since the slope of eq 8 shows that nm is equal to unity with m = 1; thus eq 3 and 5 are identical.

The structure of the ($AlCl_3$·2THF) complex may be inferred from its spectroscopic characteristics (Table I). The only probable forms are a molecular and an ionic arrangement: $AlCl_3$·2THF and [$AlCl_2$·2THF$^+$ + Cl$^-$]. The three vibrational frequencies, 510, 496, and 329 cm^{-1}, are lowered by about 100 cm^{-1} in the spectra of solutions containing $AlBr_3$ (Table I). Since the stretching Al–Cl modes are expected in this frequency range, we believe that we deal here with the three Al–Cl bands of the complex $AlCl_3$·2THF. Therefore, the unique possibility is the molecular adduct $AlCl_3$·2THF with an aluminum coordination number of five.

Such an arrangement may correspond to a cis or a trans position of the THF molecules in the trigonal bipyramid. The polarized Raman line at 150 cm^{-1} must be assigned to a bending mode of compound B. Since a totally symmetrical bending mode is expected only in the cis configuration, compound B must correspond to this model.

The strong ^{27}Al NMR peak of this molecular complex is consistent with our interpretation since its broadness indicates a low-symmetry species, and its position is intermediate between those of species including four- and six-coordinate Al atoms.[14] As far as we know, this is the first report on ^{27}Al NMR data of such a five-coordinate Al atom.

Influence of Temperature on the Structure of a 0.5 M Solution of $AlCl_3$ in Pure THF. The above analysis of the 1 M solution of $AlCl_3$ in pure THF gives evidence for equilibrium 9. The temperature dependence of the infrared and

$$2[\mathrm{AlCl_3}\cdot 2\mathrm{THF}] \rightleftarrows \mathrm{AlCl_4^-} + \mathrm{AlCl_2(THF)_4^+} \qquad (9)$$

NMR intensities (Figure 3A) shows that the features due to the molecular compound tend to disappear when the temperature *decreases*, while those of the ionic form are increasing. This means that (a) two ($AlCl_3$·2THF) complexes are brought into contact and (b) reorganization occurs which leads to the ionic structure $AlCl_4^-$ + $AlCl_2(THF)_4^+$, presumably through a temporary ion pair.

The chemical shifts of either the $AlCl_4^-$ or the molecular adduct lines do not depend upon the temperature. Therefore, the influence of coalescence processes on the observed intensities is negligible below 24 °C. The ratio R of the areas of the peaks at −63 and −102 ppm represents then the state of equilibrium 9. On the other hand, the line width of the $AlCl_4^-$ NMR signal decreases with the temperature while that of the $AlCl_3$·2THF peak increases. This denotes existence of a slow exchange process between $AlCl_4^-$ and the molecular adduct. When such an exchange occurs, the highly symmetrical anion $AlCl_4^-$ (T_d) suffers a nonsymmetrical field gradient which involves a significant quadrupolar relaxation. This leads to an increase of the correspondent line width with rising temperature. The changes of the line widths upon a temperature decrease are consistent with a slower exchange rate.

Influence of Concentration on the Structure of Solutions of $AlCl_3$ in Pure THF. The appearence of the IR and NMR spectra with decreasing concentrations of $AlCl_3$ in pure THF (Figure 3B) is surprising: while a strong IR band grows at 490 cm^{-1}, the ratio of areas of the NMR peaks at −102 and −63 ppm indicates a slight decrease of the ionic part. The weak, broad band at −9 ppm is still observed despite a relatively poor signal/noise ratio. The integrating curve shows that its area remains equal to that of the peak at −102 ppm. Furthermore, the intensities of the IR band at 510 cm^{-1} and of the cation bands at 440 and 360 cm^{-1} decrease while the intensity of the IR band at 420 cm^{-1} increases. In addition, the strong NMR peak does not shift at all but only narrows. These IR results strongly suggest the formation of an additional species (D), characterized by the bands at 490 and 420 cm^{-1}. Since the chemical shift of the main NMR band remains −63 ppm, species D must have approximatively the same chemical shift as $AlCl_3$·2THF, even if coalescence occurs.

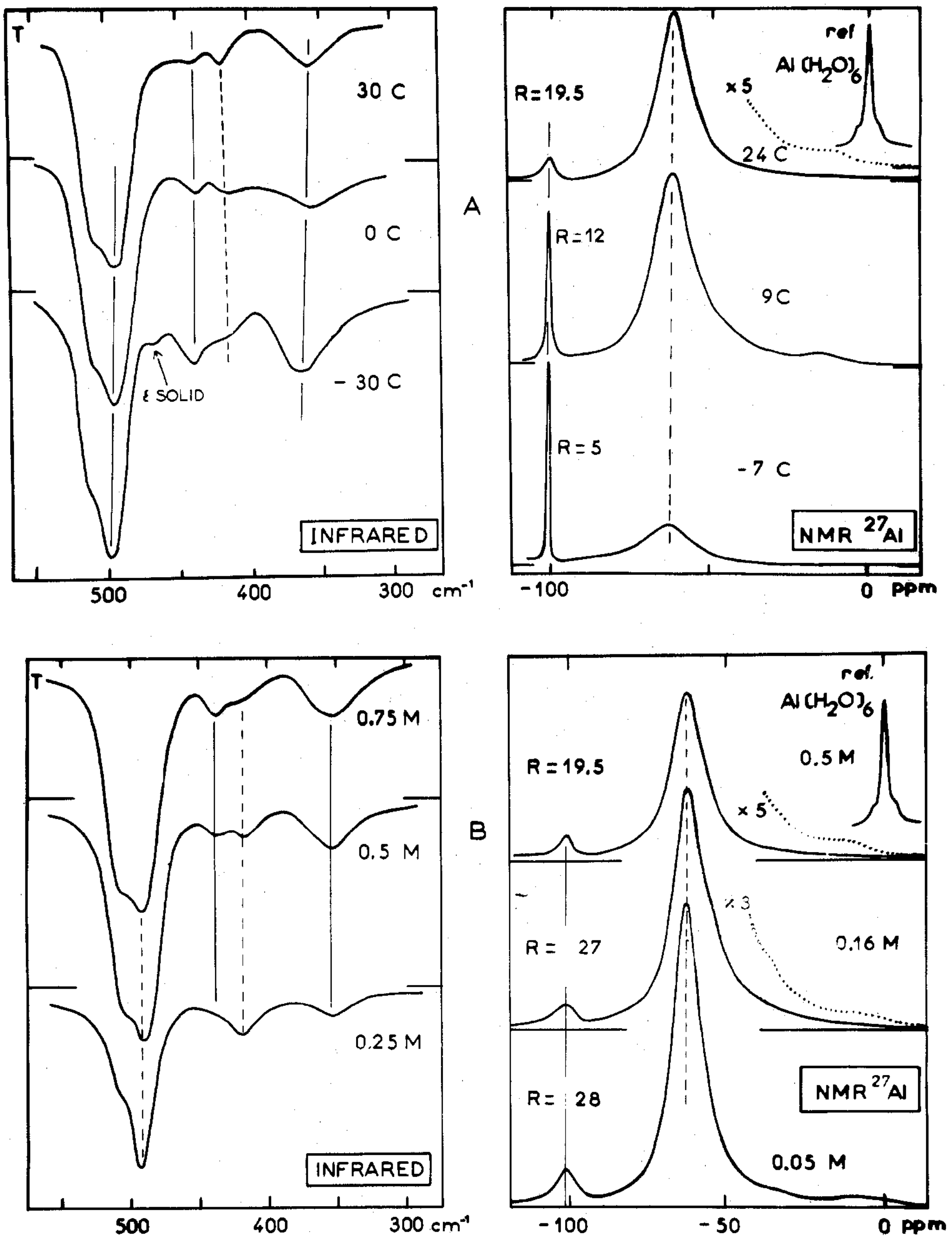

Figure 3. Modifications of the infrared and NMR spectra of $AlCl_3$ species in pure THF upon temperature (A) and concentration (B) variation. R is the ratio of peak areas due to molecular species and the $AlCl_4^-$ anion. The IR band with an arrow "ε solid" is caused by incipient crystallization on the windows. The shift between solid and solute 1:2 ionic frequencies arises from solvent effects. Dotted lines correspond to magnified spectra.

We believe that species D is not the hexacoordinated molecular adduct $AlCl_3 \cdot 3THF$. In fact, such an adduct, if it exists, would be unlikely to give rise to a peak in the range −60 ppm, since all known compounds having a hexacoordinated Al atom lead to a ^{27}Al NMR signal in the vicinity of that of $[Al(H_2O)_6]^{3+}$.[14,15]

We assume the following explanation: the new species (D) could be the trans isomer of the molecular compound $AlCl_3 \cdot 2THF$, of a distorted D_{3h} symmetry. The corresponding equilibrium is

$$cis\text{-}AlCl_3 \cdot 2THF \rightleftarrows trans\text{-}AlCl_3 \cdot 2THF \qquad (10)$$

This interpretation accounts for the unique NMR line at −63 ppm and for the single Al–Cl infrared stretching band close to 500 cm^{-1}, as observed for the *trans*-$AlCl_3 \cdot 2N(CH_3)_2$ compound.[16] The NMR line width is smaller than that of *cis*-$AlCl_3 \cdot 2THF$ due to the higher symmetry of the Al atom environment. The observed total line width at −63 ppm results from the simultaneous existence of equilibria 9 and 10.

Solutions of $AlBr_3$. The $AlBr_3$–THF system has been studied by the same method, but in a somewhat less extensive manner due to considerable experimental difficulties with the cell windows and the width of the NMR signal. The main difference is the absence of the ionic compound in all the studied solutions. Two successive equilibria (eq 11 and 12) occur in mixed solutions with CH_2Cl_2. The 1:2 complex is

$$^1/_2Al_2Br_6 + THF \xrightleftharpoons{CH_2Cl_2} AlBr_3 \cdot THF \qquad (11)$$

$$AlBr_3 \cdot THF + THF \xrightleftharpoons{CH_2Cl_2} AlBr_3 \cdot 2THF \qquad (12)$$

also observed in solutions in pure THF by infrared, Raman, and ^{27}Al NMR spectroscopy (Table I). Even in pure THF as solvent no band corresponds to the $AlBr_4^-$ anion. None of the spectroscopic features either support or contradict the cis–trans equilibrium of the 1:2 molecular adduct.

Thermodynamical Results. Although the aim of this work was not to determine the thermodynamical characteristics of the reactions, we feel that it is of some interest to give estimated values whenever possible.

1. Reaction I. The equilibrium constant for reaction I (eq 13) is given by eq 14, where c_o is the AlX_3 concentration (0.015

$$^1/_2Al_2X_6 + THF \rightleftarrows AlX_3 \cdot THF \tag{13}$$

$$k_c^{I} = (2/c_o)^{1/2} y_1 (1 - y_1)^{-3/2}\ (\text{mol L}^{-1})^{1/2} \tag{14}$$

M) and y_1 the molar fraction of the 1:1 adduct. The absorbance of the infrared band at 1064 cm^{-1} of free THF leads to the $(1 - y_1)$ value from the previously measured molar absortivity of THF. The equilibrium constants are $k_c^{I} = 89 \pm 20$ and 133 ± 21 $(\text{mol L}^{-1})^{1/2}$ for $AlCl_3$ and $AlBr_3$, respectively.

2. Reaction II. For reaction II (eq 15), we derive eq 16,

$$AlCl_3 \cdot THF + THF \overset{CH_2Cl_2}{\rightleftarrows} cis\text{-}AlCl_3 \cdot 2THF \tag{15}$$

$$k_c^{II} = y_2(1 - y_2)^{-1}[c_o(x - 1 - y_2)]^{-1}\ (\text{mol}^{-1}\text{ L}) \tag{16}$$

in which $c_o = 0.015$ M and $1 < x \leq 75$ denote the same quantities as above, and y_2 is the molar fraction of the 1:2 adduct. The value of the equilibrium constant of eq 15 could a priori be derived from either the IR data or the NMR results. Comparison of eq 7 and 8 leads to the expression

$$k_c^{II}[\epsilon_{510}/\epsilon_{546}] = 15.22\ \text{L mol}^{-1} \tag{17}$$

The values of the absorbances (see Table II) suggest the crude assumption that $\epsilon_{510}/\epsilon_{546} \simeq 1$. Then the k_c^{II} value would be equal to about 15 L mol^{-1}.

In fact, the calculation of k_c^{II} on the basis of our NMR results is not feasible since we observe only one band for both isomers of the molecular 1:2 compound. On the other hand, the infrared results allow this calculation because the band at 510 cm^{-1} is characteristic of the cis 1:2 compound and the condition $1 < x \leq 75$ leads to low concentrations of the C and D compounds.

3. Reaction III. For reaction III (eq 18) we derive eq 19,

$$2[AlCl_3 \cdot 2THF] \rightleftarrows AlCl_4^- + Al(THF)_4Cl_2^+ \tag{18}$$

$$k_c^{III} = y_3^2(1 - 2y_3)^{-2} = R^{-2} \tag{19}$$

in which y_3 is the ionic fraction. The integration of the ^{27}Al NMR peaks at 24 °C yields directly the ratio R. We found that $R = 19.5 \pm 2$ and, thus, the equilibrium constant $k_c^{III} = (2.6 \pm 0.3)10^{-3}$.

An estimate of the free enthalpy ΔG_R of reaction III can be derived from the variation of k_c^{III} with temperature, using the Arrhenius law. The R values are collected in Figure 3A; the resulting ΔG_R enthalpy = 12 ± 1 kcal mol^{-1}.

From broadening of the $AlCl_4^-$ NMR line with temperature, we obtain the exchange rate and the activation energy ΔG^*. The rate constant $k_e(T)$ is written

$$k_e(T) = \pi(\delta_T - \delta) \tag{20}$$

where δ is the line width when no exchange occurs, and δ_T is the experimental line width at temperature T.[17,18] The δ value, under the same experimental conditions, may be assumed to be equal to the $AlCl_4^-$ line width in the $AlCl_3$–CH_3CN system where no exchange occurs[19] (for this ion $\delta = 2$ Hz). Table III gives the numerical data. When the $k_e(T)$ values are plotted vs. $1/T$, a fairly straight line is obtained, and the three possible couples of points yield the mean ΔG^* value: 15 ± 1.5 kcal mol^{-1}. This value is greater than the absolute value of the free enthalpy of reaction III; this is indeed the consequence of a genuine barrier in the exchange process.

Table III. ^{27}Al NMR Line Widths for the Anion $AlCl_4^-$ at Various Temperatures in THF

δ_T, Hz	90	25	6
T, K	297	282	264

Conclusion

The striking result of the above study is the essentially molecular composition of solutions of AlX_3 in THF in opposition to the ionic nature of the solid compound ($AlX_3 \cdot 2THF$).

A number of solute species have been identified, and reactions I–IV have been investigated. ($AlBr_3$ solutions lead only

$$^1/_2Al_2X_6 + THF \rightleftarrows AlX_3 \cdot THF \tag{I}$$

$$AlX_3 \cdot THF + THF \rightleftarrows AlX_3 \cdot 2THF \tag{II}$$

$$2[AlCl_3 \cdot 2THF] \rightleftarrows AlCl_4^- + AlCl_2(THF)_4^+ \tag{III}$$

$$cis\text{-}AlCl_3 \cdot 2THF \rightleftarrows trans\text{-}AlCl_3 \cdot 2THF \tag{IV}$$

to equilibria I and II.)

These various complexes probably do not have the same behavior as catalyst reagents, and this may explain the wide range of reactions in which such systems may be used.

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Registry No. A, 15283-71-3; B, 64281-57-8; C, 64200-55-1; D, 15615-14-2; $AlBr_3 \cdot THF$, 15283-67-7; $AlBr_3 \cdot 2THF$, 14221-13-7; ^{27}Al, 7429-90-5.

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