bonding leads to the prediction of an electronic preference for *cis*-M(dppm)$_2$Cl$_2$. In idealized D_{4h} symmetry for the trans isomer the t$_2$ orbitals split into e$_g$(*xz*, *xy*) and b$_{2g}$(*xy*) and in the C_2 symmetry of the cis isomer, the t$_2$ orbitals become a$_1$(*yz*) and a$_2$(*xy*), b$_2$(*xz*). For the two isomers it is easily shown that the number of stabilizing $d\pi \rightarrow d(P)$ interactions and destabilizing $d\pi \leftarrow p(Cl)$ interactions are the same. However, for the cis isomer there is an additional stabilization. For the cis isomer there are two axial Cl-M-P groupings in place of the Cl-M-Cl and P-M-P groupings of the trans isomer. The net effect leads to enhanced back-bonding with phosphorus through the common metal d orbital via a $p\pi(Cl) \rightarrow d\pi(Ru) \rightarrow d\pi(P)$ interaction as has been recognized for d^8 square-planar complexes.[11]

Upon oxidation to Ru^{III}(dppm)$_2$Cl$_2^+$ the trans isomer becomes thermodynamically favored. This could arise if steric repulsion between ligands is important as has been suggested[7c] for other isomerization reactions or if the trans cation, which has a formally doubly degenerate symmetrical ground state, undergoes a Jahn-Teller distortion. The latter effect, if it exists, would be small since no such static distortion has been observed for Ru(NH$_3$)$_6^{3+}$.[12] It is interesting to note that irradiation of the d-d manifold in *cis*-Ru^{II}(dppm)$_2$Cl$_2$, which labilizes metal-ligand bonds, has the effect of removing an electron from a $d\pi$ level, decreasing π-bonding stabilization. In a sense the excited state from which cis → trans photoisomerization occurs resembles the oxidized cis isomer and similar factors may govern the isomeric distributions in both the oxidative and the photoisomerization reaction.

Finally, isomerization reactions that exhibit all three pathways, thermal, photochemical, and electrochemical, may be a common feature of transition-metal chemistry, but this will only be known by systematic electrochemical investigations of cis-trans and *fac-mer* isomeric pairs, which exhibit thermal and photochemical isomerizations.

Acknowledgments are made to the Deparment of Energy under Grant No. DE-A505-78ER06034 for support of this research and to Mr. E. Kober for helpful discussions.

Registry No. *trans*-Ru(dppm)$_2$Cl$_2$, 38800-82-7; *cis*-Ru(dppm)$_2$Cl$_2$, 79982-54-0; *cis*-Ru(bpy)$_2$Cl$_2$, 19542-80-4; *cis*-[Ru(dppm)$_2$(CH$_3$CN)Cl](PF$_6$), 79953-54-1; *trans*-Os(dppm)$_2$Cl$_2$, 79953-55-2; *cis*-Os(dppm)$_2$Cl$_2$, 79982-55-1; *cis*-Os(bpy)$_2$Cl$_2$, 79982-56-2; *cis*-[Os(dppm)$_2$(CH$_3$CN)Cl](PF$_6$), 79953-57-4; tetra-*n*-butylammonium hexachloroosmate(IV), 58590-70-8.

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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. 1. Aluminum Chloride-Acetonitrile Solutions

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

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The AlCl$_3$-CH$_3$CN system has been investigated by infrared and Raman spectroscopy and by ^{35}Cl and ^{27}Al NMR spectrometry over the [CH$_3$CN]/[AlCl$_3$] molar ratio range 5.6-80. The system consists mainly of ionic complexes that share the same anion, AlCl$_4^-$. Three octahedral cations have been characterized: Al(CH$_3$CN)$_6^{3+}$, AlCl(CH$_3$CN)$_5^{2+}$, and AlCl$_2$(CH$_3$CN)$_4^+$. A new species, the Al(CH$_3$CN)$_5^{3+}$ cation, was found in concentrated solutions. The identification of the cations was made on the basis of their individual ionic charge and their solvation number.

Introduction

Among the binary systems of aluminum halides in organic bases, AlCl$_3$-CH$_3$CN solutions have been extensively studied, but the chemical structure of the dissolved species is still unresolved. Previous studies suggest that different species are in equilibrium, which may be explained by the competition between Cl$^-$ and CH$_3$CN ligands which leads to exchange processes.

Up to now, various techniques have been used to study these complexes: conductivity,[2,3] polarography,[4] ion exchange,[5] infrared and Raman spectroscopy,[6-8] and aluminum-27 NMR spectrometry;[7-13] ref 13, which appeared at the time of the writing of this paper, will be particularly commented on below. All the results of the above papers show that these solutions are mainly ionic, but if the AlCl$_4^-$ anion is generally identified unambiguously, this is not the case for the cationic part. Furthermore, ref 13 suggests that a small amount of the neutral species AlCl$_3$·CH$_3$CN$_2$ is present.

Recent results obtained in our laboratories on solutions of AlBr$_3$ in CH$_3$CN[14] encouraged us to reinvestigate AlCl$_3$ in

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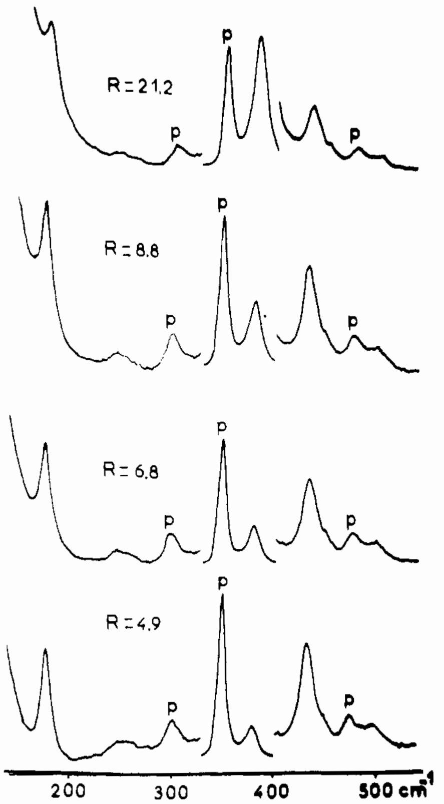

Figure 1. Effect of concentration on the Raman spectra of aluminum chloride in acetonitrile. The ordinate scale in the central frequency range is divided by 5. Polarized lines are marked p.

this solvent. In this work, using infrared, Raman, and NMR spectroscopic techniques on 0.2–3.5 M solutions, we have determined the ionic charge and the solvation number of each species formed in these solutions. Finally, we have deduced the chemical structure of these complexes.

Experimental Section

Preparation of the Solutions. Aluminum trichloride and acetonitrile were purified as previously described.[14] AlCl$_3$ was dissolved in CH$_3$CN at low temperature under vacuum. Solutions for the Raman measurements were prepared by dissolution of solid AlCl$_3$·2CH$_3$CN that had been purified by recrystallization.[16] The composition of each solution is defined by the molar ratio $R = [\mathrm{CH_3CN}]/[\mathrm{AlCl_3}]$.

Raman spectra were recorded between 100 and 550 cm^{-1} with a Coderg PHO apparatus powered by an Ar$^+$ laser tuned to 488.0 nm. It was necessary to accumulate between 150 and 400 spectra, depending upon the concentration of the solutions. The resulting averaged spectrum was smoothed, and the base line was corrected to eliminate the fluorescence background. Samples were contained in sealed glass tubes.

Infrared spectra were recorded between 350 and 4000 cm^{-1} on a Nicolet MXl system. To avoid the interactions of the solutions with ICs or AgBr windows, we used a cell built entirely of polyethylene and poly(tetrafluoroethylene).[14]

NMR Spectra. ^{27}Al and ^{35}Cl NMR spectra were recorded on a Bruker WH90C at 23.45 and 8.82 MHz, respectively. High-field spectra were obtained on a Bruker WH250 at 65.14 MHz. The experimental conditions were the same as previously used.[14] ^{27}Al chemical shifts are referred to Al(H$_2$O)$_6^{3+}$. We would like to point out the difficulties met in recording accurate spectra in which narrow lines (3 Hz) and broad bands (1100 Hz) are simultaneously observed. Our previously described procedure[14] was obtained after careful essays and calibrations. A supplementary difficulty was encountered in the measurement of the area of wide bands: the integration domain being necessarily limited, the apparent measured area of this type of line is less than its real value. An estimate of the error is easily calculated for a Lorentzian line. The total area S_∞ after an integration from $-\infty$ to $+\infty$ should be $S_\infty = (\pi/2)h\Delta\nu_{1/2}$, where h is the height of the line and $\Delta\nu_{1/2}$ its width at half-height. The measured area between

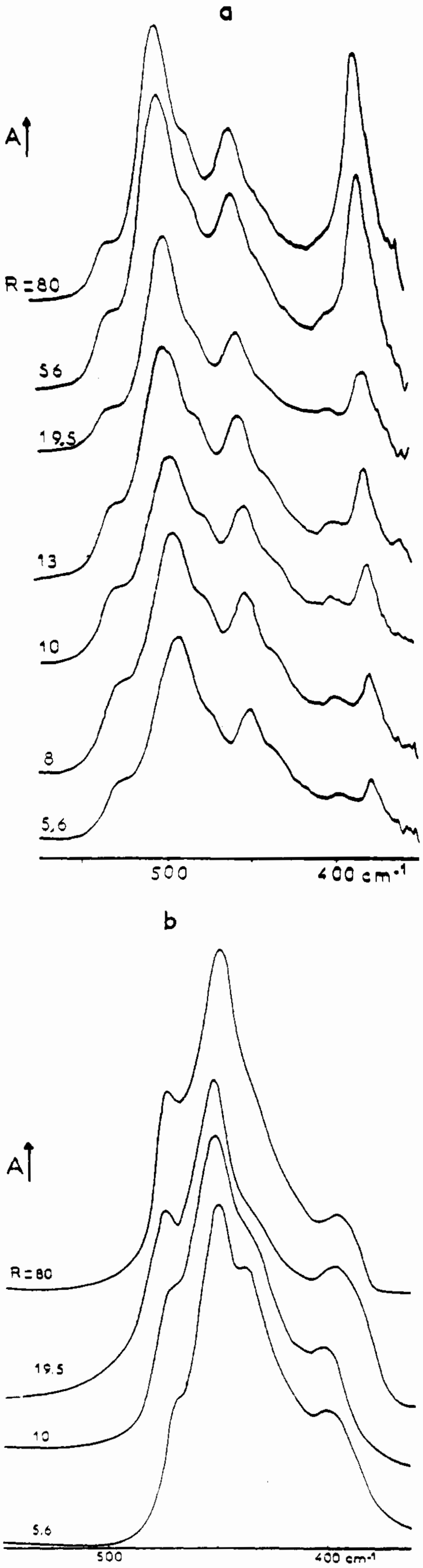

Figure 2. Effect of concentration on the infrared spectra of aluminum chloride in acetonitrile (A = absorbance): (a) spectra as recorded; (b) result of the computer subtraction of AlCl$_4^-$ and of the solvent.

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Table I. Spectroscopic Data Related to Identified Complex Species in CH_3CN Solutions of $AlCl_3$

	$Al(CH_3CN)_6^{3+}$ (A) O_h	$AlCl(CH_3CN)_5^{2+}$ (B) C_{4v}	$AlCl_2(CH_3CN)_4^+$ (C) C_{2v}	$Al(CH_3CN)_5^{3+}$ (D) C_{4v}	$AlCl_3 \cdot CH_3CN$	$AlCl_4^-$ T_d
stoichiometry[a]	3/2	5/3	2	5/4	1	
infrared, cm^{-1}	470 (8)[b] T_{1u}[c]	450 (10) E	475 (9)	440 (25) A_1		495 (0)[d] T_2
		400 (10)				
Raman, cm^{-1}		477 (2)[e] A_1				502 (0) T_2
		451 (8) E				352 (0)[e] A_1
		436 (25) B_1				180 (0) T_2
		304 (11)[e] A_1				
^{27}Al NMR						
δ	−34	−24	−14	−12 to −10	+96	+102
$\Delta\nu_{1/2}$, Hz	15	660–170[d]	255–210[d]	1130–180[d]	45	3

[a] $(CH_3CN)/(AlCl_3)$ in neutral complex; see text. [b] Isotopic shift ($\nu_H - \nu_D$) for the perdeuterated species. [c] Assignment in terms of symmetry types. [d] The line width of this band decreases when *R* increases. [e] Polarized Raman line.

$-L$ and $+L$ is given by $S_{2L} = h\Delta\nu_{1/2} \arctan (2L/\Delta\nu_{1/2})$. In our measurements, the integration domain is limited to 6000 Hz by the sweep width; the above relations show that for a line width of about 200 Hz the error in our case is about 2%, but for larger line widths, this error may reach 10%. We have taken into account this correction in all measurements.

Results and Discussion

Vibrational Spectroscopy. Some IR bands arising from bonded CH_3CN were detected above 600 cm^{-1}. They are consistent with our previous results on solid compounds,[15] but they do not allow a detailed discussion of the structure of the dissolved complexes.

The infrared and Raman bands found around 380 cm^{-1} come from free acetonitrile (Figures 1 and 2). All infrared spectra display a strong band at 494 cm^{-1} and a shoulder at about 530 cm^{-1}. Similarly, we observe in all Raman spectra an intense and polarized sharp line at 350 cm^{-1} and a depolarized one at 182 cm^{-1}. These four bands allow an unambiguous identification of the $AlCl_4^-$ anion.[17] The frequencies of these lines do not shift when normal acetonitrile is replaced by deuterated acetonitrile.

The only feature of these spectra that needs comment concerns the line width of the infrared band at 494 cm^{-1} ($\nu_d(AlCl_4^-)$). It increases from 25 cm^{-1} for the solution corresponding to $R = 80$ to 40 cm^{-1} for $R = 5.6$. This is likely due to changes in the surroundings of $AlCl_4^-$ when the concentration of $AlCl_3$ increases. Two hypotheses may be proposed to explain this result: the formation of ion pairs, or an interaction with the solvent as found for the ClO_4^-–CH_3CN system.[18] The first explanation may lead to a maximum perturbation for the highest concentration of $AlCl_4^-$ (low *R*). The second explanation leads to the opposite conclusion. Consequently, we think that the formation of ion pairs is the most important phenomenon.

It is questionable whether the anion $Al_2Cl_7^-$ is present in the solutions or not. Its intense characteristic Raman line at 315 cm^{-1},[19] which is polarized, has not been detected. We conclude that if this anion is present in the solutions, its concentration is very low and may be neglected.

The remaining infrared (475, 450, 440, 400 cm^{-1}) and Raman (477, 451, 436, 304 cm^{-1}) bands that have been observed arise from either cationic or molecular species. Except for the lines due to free acetonitrile, the spectra are not deeply modified when *R* is varied (Figures 1 and 2). In order to facilitate the analysis of the infrared spectra, we executed for each *R* value a computer subtraction of the bands due to $AlCl_4^-$ and to the solvent (Figure 2). There then appears a strong band at 450 cm^{-1} and a medium band near 400 cm^{-1}, which are observed whatever the *R* value. The intensity of the weak side peaks at 475 and 440 cm^{-1} increases and decreases, respectively, when *R* is increased. We may conclude then that one species is abundant and that two other complexes exist at much lower concentrations.

The Raman spectra do not change with concentration. We think that we observe only the most important species, the lines of the others being too weak or hidden by more intense bands. Comparison of the spectra of these solutions with those of the well-defined solids $AlCl_3 \cdot C_5H_5N$,[20] $[AlCl_4^-, AlCl_2(C_5H_5N)_4^+]$,[21] $[3AlCl_4^-, Al(CH_3CN)_6^{3+}]$,[15] and $[2AlCl_4^-, Al(CH_3CN)_5Cl^{2+}]$[16] and the isotopic effects (Table I) suggest that the main species is the cation $AlCl(CH_3CN)_5^{2+}$. The polarization of the Raman lines at 477 and 304 cm^{-1} confirms our previous results; they correspond respectively to the ν(Al–Cl) and ν(Al–N) modes of this cation.

NMR Spectra. General Features. All ^{27}Al NMR spectra display superimposed broad bands at high field near −25 ppm and an intense narrow line ($\Delta\nu_{1/2} = 3$ Hz) at +102 ppm (Figure 3a). According to the literature,[22,23] this last resonance is assigned to $AlCl_4^-$. Between 0 and 100 ppm, only a weak line is detected at +96 ppm in the spectra recorded at 65.14 MHz. Its line width is 45 Hz. Integration curves show that the concentration of this species always remains below 1% of the overall concentration of aluminum species. The authors of ref 13 have also found this line, but they found a stronger line as well, at +87 ppm, which has never been observed in our experiments. We propose that the resonance at +96 ppm arises from the 1:1 molecular complex $AlCl_3 \cdot CH_3CN$ since its chemical shift is very close to that of the analogous complexes $AlCl_3 \cdot CH_3NO_2$ (at 97 ppm[24]) and $AlCl_3 \cdot C_4H_8O$ (at 94 ppm[25]).

In order to make sure that we observed all aluminum species present in the solutions and that no broad band escaped our observations, we compared the intensities observed in CH_3CN solutions of $AlCl_3$ with the intensity of an $Al(D_2O)_6^{3+}$ sample of known concentration. This procedure is analogous to that used in our previous work.[14]

Since our analysis is based on the balance between the ionic charges of each species, we tried to observe Cl^- by using ^{35}Cl NMR. All our attempts to detect this anion failed. To make this result significant, we recorded the signal of Cl^- in the same conditions in a $LiCl/CH_3CN$ solution at low concentration. The resonance is easily observed. We therefore conclude that

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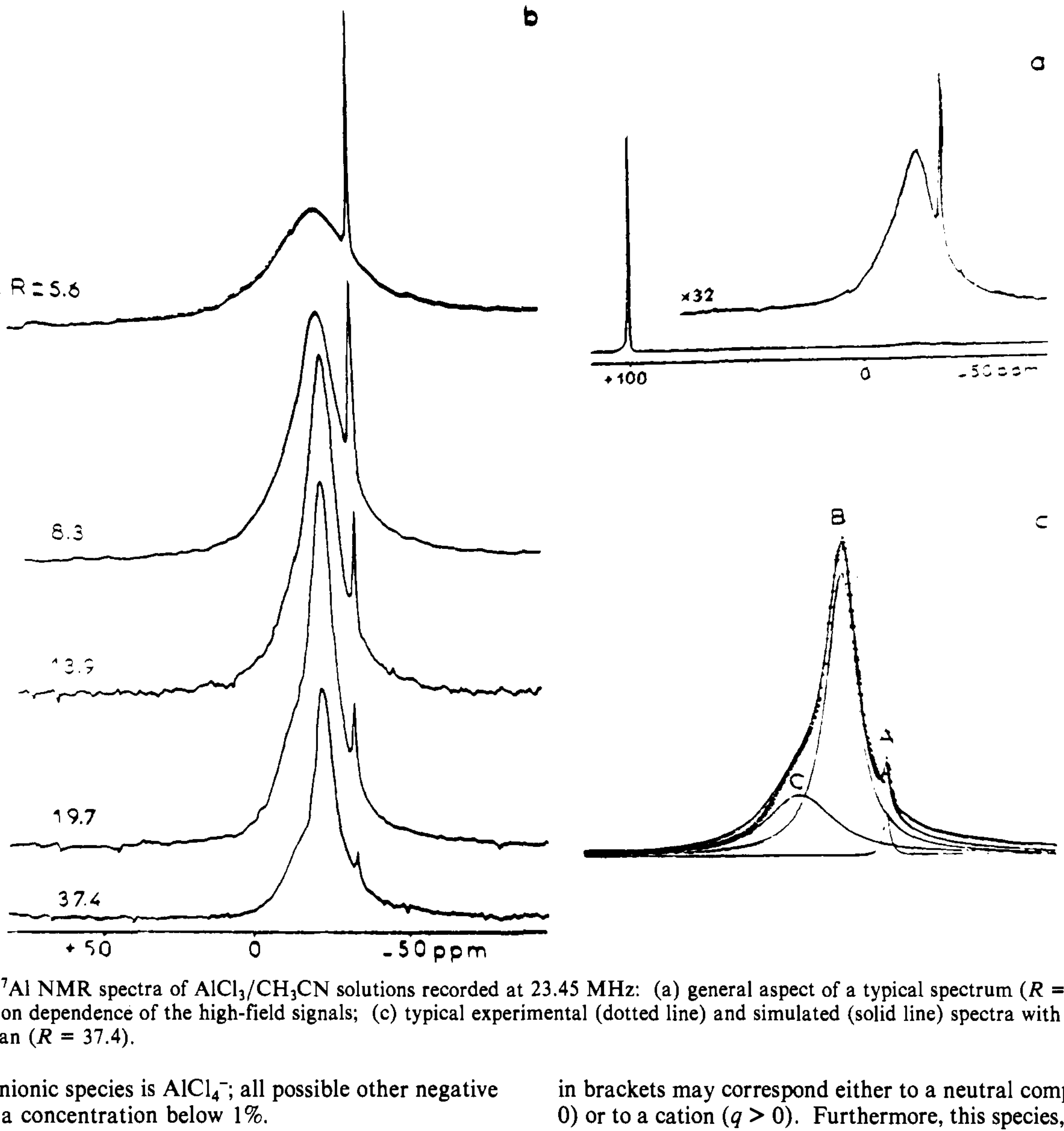

Figure 3. ^{27}Al NMR spectra of $AlCl_3/CH_3CN$ solutions recorded at 23.45 MHz: (a) general aspect of a typical spectrum ($R = 6.3$); (b) concentration dependence of the high-field signals; (c) typical experimental (dotted line) and simulated (solid line) spectra with A, B, and C Lorentzian ($R = 37.4$).

the only anionic species is $AlCl_4^-$; all possible other negative ions have a concentration below 1%.

Method of Interpretation. In order to identify the different species arising in the high-field range of chemical shifts, we used the procedure described previously in our study of CH_3CN solutions of $AlBr_3$.[14] The method is based upon the determination of the relative concentration of each complex and of their ionic charge. It is evident that the mean positive charge of all the cationic species must balance the negative charge carried by $AlCl_4^-$.

There are two ways to obtain the mean charge $\bar{q}$ of the cations: first, by measuring the ratio of the area corresponding to the high-field signals to that of $AlCl_4^-$; second, by dealing with the intensities of each high-field band. These intensities are obtained through a curve analysis in several Lorentzian lines, and an ionic charge is assigned to each of them. When the R value varies, this procedure leads to a calculation of $\bar{q}$ for each R value and yields the changes in concentration of each species. The two values obtained for $\bar{q}$ must be equal and vary similarly when R is modified.

The second step of the analysis is the calculation of the solvation number n of each complex corresponding to the general formula

$$\{[Al_mCl_{m(3-q)}CH_3CN_{m(N-3+q-(b/m))}]^{mq+},\ mqAlCl_4^-\}$$

1

This rather cumbersome formula will make easier the discussion of our results if one considers that the part included in brackets may correspond either to a neutral complex ($q = 0$) or to a cation ($q > 0$). Furthermore, this species, in which N stands for the coordination number of the Al atoms, may have a polynuclear framework in which m Al atoms are bridged by b chlorine atoms; if $m > 1$, we have $(m - 1) < b < m(3 - q)$. An example of a similar binuclear species is $[Al_2(OH)_2(H_2O)_8]^{4+}$,[26] where OH and H_2O replace Cl and CH_3CN, respectively, and where $m = 2$, $q = 2$, $N = 6$, and $b = 2$. In a mononuclear complex, $m = 1$ and $b = 0$, and then the formula accounts for the well-known expressions $(AlCl_xL_{6-x})^{(3-x)+}$,[8,14–16,21,25,27] $(AlCl_xL_{5-x})^{(3-x)+}$,[25,28,29] and $(AlCl_xL_{4-x})^{(3-x)+}$.[15,20,24,25] The solvation number n is then easily expressed as

$$n = (N - 3 + q - b/m)/(1 + q) \qquad (1)$$

The species with the greater solvation number n appears as R increases, and the evolution of the relative concentrations of the different complexes allows us to classify them according to n. The last evident conditions are $4 \leq N \leq 6$ and $0 \leq q$

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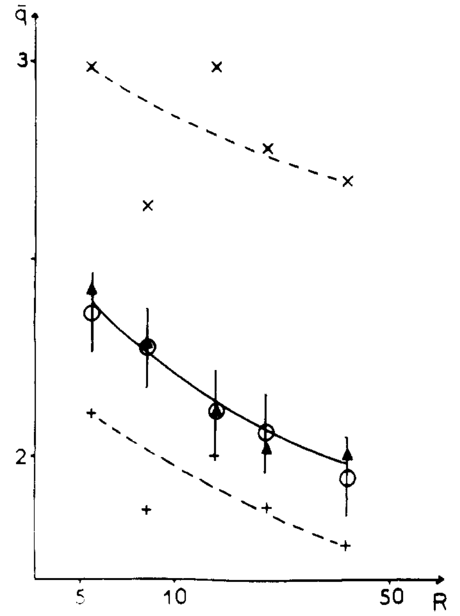

Figure 4. Plot of the average ionic charge $\bar{q}$ vs. molar ratio R: (○) experimental average charge (uncertainties are designated by a bar); (×) calculated charge with $q_A = 3+$, $q_B = 3+$, and $q_C = 2+$; (+) calculated charge with $q_A = 3+$, $q_B = 2+$, and $q_C = 1+$ (previous assignment in ref 8); (▲) calculated charge from 65.14-MHz data (see text).

≤ 3. This procedure leads to the straightforward determination of the chemical structure of all the complexes detected.

Results

The high-field part of the 23.45-MHz spectra (Figure 3a,b) shows bands at −34, −23, and −13 ppm. The deconvolutions are very difficult to perform, and the calculated spectra do not fit the experimental curves as satisfactorily as in our previous work:[14] a typical example of this curve analysis is shown in Figure 3c. From these results, the mean-square value of the cationic charge $\bar{q}$ is calculated and plotted in Figure 4 as a function of R. A poor agreement with the experimental results is observed whatever the assumptions concerning the charge of each species; in particular, the assignment proposed in ref 8 does not fit the experimental curve. This result suggested that other species are involved and led us to record spectra at a higher frequency, that is, at 65.14 MHz.

The spectra are presented in Figure 5a. They display bands at −34 (A), −24 (B), −14 (C), and −11 (D) ppm; the last band is slightly shifted toward low field by about 2 ppm as R increases, a result consistent with that of ref 13. The deconvolutions presented in Figure 5b and in Table II (Supplementary Material) show that the experimental spectra are well fitted with calculated spectra based upon four bands. The relative areas of each Lorentzian line are reported in Figure 5c. We then conclude that there are four different species that are responsible for the high-field signal.

We then tried to fit the experimental mean charge $\bar{q}$ by using different values of q for each detected complex. The only satisfactory set is

$$q_A = 3+ \qquad q_B = 2+ \qquad q_C = 1+ \qquad q_D = 3+ \tag{2}$$

These values lead to a very good agreement between the experimental and calculated $\bar{q}$ curves (Figure 4). Our assignment only partially agrees with the results of Wehrli and Hoerdt.[13] If one assumes their interpretation, the cationic charge is mainly that of $AlCl(CH_3CN)_5^{2+}$, which leads to $\bar{q} \simeq 2$ and is inconsistent with the value 2.9 found by these authors.

Since increasing values of R must yield complexes with greater solvation numbers n, evolution of the ratios of concentrations (Figure 5d) leads to the following order for the n values:

$$n_D < n_A < n_B < n_C \tag{3}$$

The charge $q = 3+$ of the cations A and D implies the lack of bridging Cl atoms and yields a mononuclear structure with the formula $Al(CH_3CN)_N^{3+}$. In this case, relation 1 is simplified as $n = N/4$ and relation 3 gives $N_D < N_A$. Since the quadrupolar contribution to relaxation of the Al nuclei only vanishes when the environment of the Al atom corresponds to a cubic point group symmetry,[22,23] species A ($\Delta\nu_{1/2} = 15$ Hz) must have a tetrahedral or octahedral framework. Thus, the only possibility is $Al(CH_3CN)_6^{3+}$ ($N_A = 6$; $n_A = 1.5$); as far as we know, this result is the first direct demonstration for the assignment currently reported in the literature.[22,23] Cation D may be $Al(CH_3CN)_4^{3+}$ or $Al(CH_3CN)_5^{3+}$. Its coordination number is unlikely to be 4 since all chemical shifts of tetrahedral species, except AlI_4^-, are known to lie in the range +40 to +150 ppm.[22,23] The only remaining hypothesis gives $Al(CH_3CN)_5^{3+}$. This assignment disagrees with the previous interpretation,[13] but it is the only one that may account simultaneously for high values of $\bar{q}$ (2.43) and for the order of solvation numbers. As far as we know, this is the first report of such an unmixed five-coordinate Al atom. Cation B, with $q_B = 2+$, corresponds to a solvation number greater than 1.5. Under these conditions, all polynuclear species lead to values of N_B greater than 6, whereas a mononuclear species requires $N_B > 5.5$ only. This is $AlCl(CH_3CN)_5^{2+}$ as previously assigned.[13] Its solvation number is $n_B = 1.66$.

Species C, with $q_C = 1+$ and $n_C > 1.66$, may be $AlCl_2(CH_3CN)_4^+$ or the dinuclear cation $Al_2Cl_4(CH_3CN)_7^{2+}$; all different assumptions lead to $N_C > 6$ or $n_C < 1.66$. We think that a dinuclear species, if formed, may appear not in dilute solutions but in concentrated ones. As we observe that the concentration of C increases with R, the $AlCl_2(CH_3CN)_4^+$ cation is the most likely ion that may account for our results. This is also the assignment suggested by Wehrli and Hoerdt.[13]

We can summarize the different equilibria of the solvolysis of $AlCl_3$ in CH_3CN by reactions 4–6.

$$Al(CH_3CN)_5^{3+} + CH_3CN \rightleftharpoons Al(CH_3CN)_6^{3+} \tag{4}$$

$$3Al(CH_3CN)_6^{3+} + AlCl_4^- + 2CH_3CN \rightleftharpoons 4AlCl(CH_3CN)_5^{2+} \tag{5}$$

$$2AlCl(CH_3CN)_5^{2+} + AlCl_4^- + 2CH_3CN \rightleftharpoons 3AlCl_2(CH_3CN)_4^+ \tag{6}$$

In our previous work on the solvolysis of $AlBr_3$ in CH_3CN,[14] we verified that the symmetry and the chemical shifts of the different octahedral species may be predicted empirically from a model based on pairwise interactions.[31] We can also apply this model to the $AlCl_3$ solutions, but the criterion based on unequal intervals between chemical shifts is not verified (Table I). Thus it is difficult to choose between the cis and trans isomers for $AlCl_2(CH_3CN)_4^{2+}$. We think that the steric hindrances due to an AlBr or an AlCl bond are similar[32,33] and that the cis form should be the more stable in this case too. The pairwise parameters may be then calculated: $\delta_{N-N} = -2.83$, $\delta_{N-Cl} = -0.33$, and $\delta_{Cl-Cl} = 2.13$.

In the above discussion of the vibrational spectra, we pointed out that the $AlCl_4^-$ anion is disturbed and we ascribe this effect to the formation of ion pairs in concentrated solutions. This analysis is consistent with the ^{27}Al NMR data: the line widths of the bands due to the cations $Al(CH_3CN)_5^{3+}$ and $AlCl(CH_3CN)_5^{2+}$ drastically decrease when R increases. This

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(32) R. J. Gillespie, *Can. J. Chem.*, **39**, 318 (1961).
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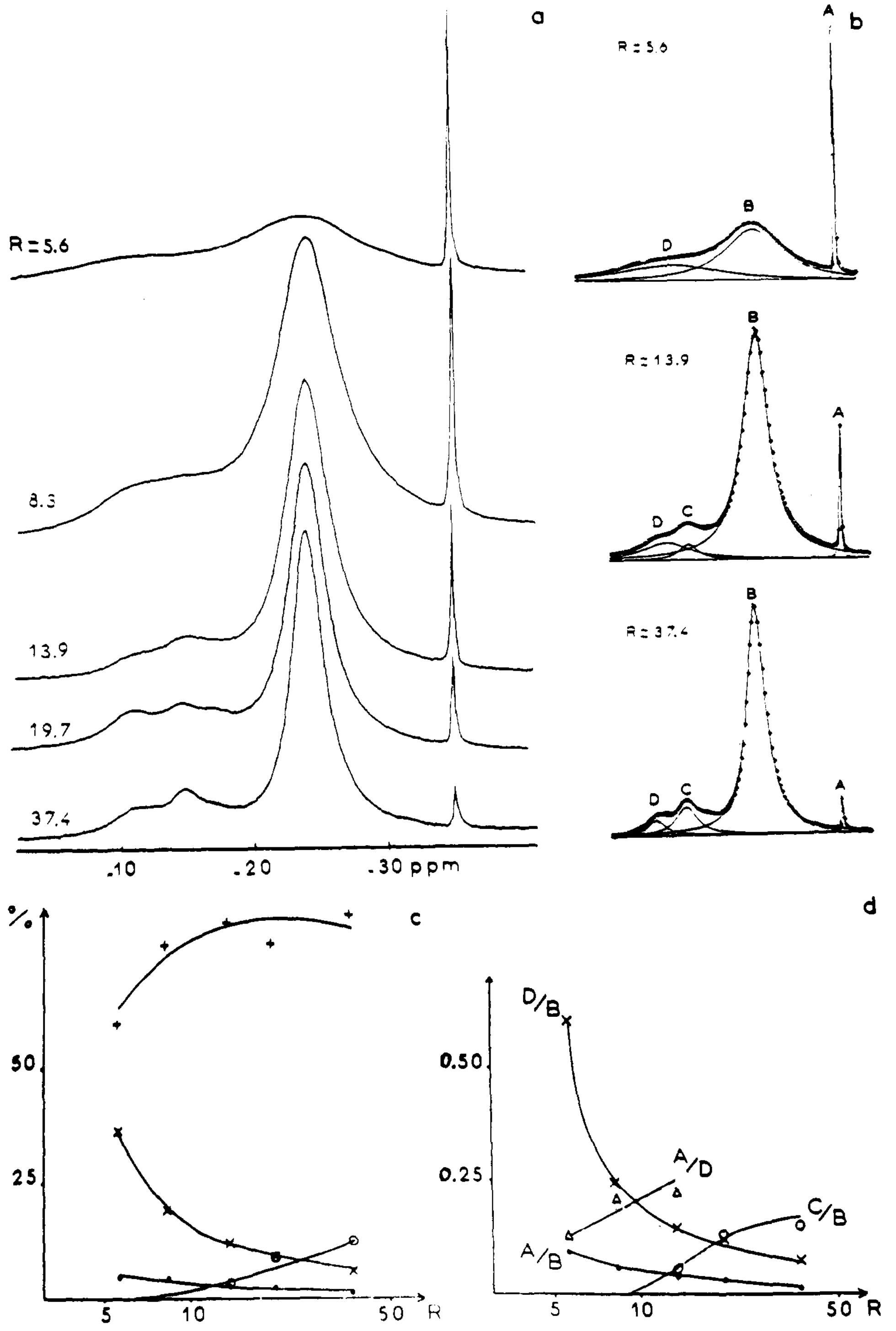

Figure 5. ^{27}Al NMR spectra of $AlCl_3/CH_3CN$ solutions recorded at 65.14 MHz: (a) concentration dependence of the high-field signals; (b) experimental (◊) and simulated (—) spectra with A, B, C, and D Lorentzian for R = 5.6, 13.9, and 37.4; (c) plot of the percentage of each high-field species vs. molar ratio R (●, +, O, and × stand for A, B, C, and D species, respectively); (d) plot of the ratios of concentrations vs. molar ratio R.

effect does not arise from a change of the viscosity since the lines at +102 and −34 ppm always keep the same narrow width (Figure 5 and Tables I and II).

The analysis of the infrared spectra may now be completed. The intensity of the IR band at 475 cm^{-1} increases with R with respect to the band at 450 cm^{-1} due to $AlCl(CH_3CN)_5^{2+}$ (Figure 2). This band must therefore be assigned to the species of which the concentration increases with R, namely, $AlCl_2(CH_3CN)_4^+$. Nevertheless, at low R values, the concentration of this cation is low; the shoulder near 470 cm^{-1} may correspond to the stretching mode $\nu_d(AlN_6)$ of the $Al(CH_3CN)_6^{3+}$ cation, which is expected at this frequency.[15] The last infrared band, at 440 cm^{-1} (Figure 2), which appears at high concentration may be assigned to one of the stretching modes ν(Al–N) of the D cation, $Al(CH_3CN)_5^{3+}$. The three species A,[15] B,[16] and D (Table I) display a stretching mode close to 440 cm^{-1} and show similar frequency shifts due to deuteration. This result suggests that we are dealing with three modes that correspond to analogous vibrational normal coordinates. The expression of vibrational coordinates, according to Wilson's method[34] for the AlN_6 (O_h), AlN_5Cl (C_{4v}), and AlN_5 (D_{3h} or

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[34] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955.

C_{4v}) frameworks and correlation tables, shows that only the C_{4v} geometry for cation D is likely to account for this result. Thus, this pentacoordinated species would consist of a square-based pyramid.

Conclusion

Following our previous work on $AlBr_3/CH_3CN$ and using the same procedure, we have identified the main species that are formed by the solvolysis of $AlCl_3$ in CH_3CN.[35] This system is more complex than the first one. The use of the concept of "mean cationic charge" is of the greatest interest in the study of systems that contain several ionic species. Our work also demonstrates the use of high-field NMR spectrometers for the study of complex solutions: the 23.45-MHz spectra do not make possible a self-consistent analysis of all the equilibria involved in the $AlCl_3/CH_3CN$ mixtures. The study of $AlCl_3$ dissolved in binary mixtures is in progress by using the above results and will be published later.

Acknowledgment. We are indebted to Professor Lascombe for helpful discussions, to the Nicolet-France Co. for the loan of the MX-1 instrument, and to Dr. Brevard of Bruker-France for the high-field NMR spectra.

Registry No. $AlCl_3$, 7446-70-0; CH_3CN, 75-05-8; $Al(CH_3CN)_5^{3+}$, 80063-19-0; $Al(CH_3CN)_6^{3+}$, 25159-95-9; $AlCl(CH_3CN)_5^{2+}$, 60475-07-2; $AlCl_2(CH_3CN)_4^+$, 45146-22-3; $AlCl_3{\cdot}CH_3CN$, 20481-47-4; $AlCl_4^-$, 17611-22-2.

Supplementary Material Available: Table II (NMR data at 65.14 MHz) (1 page). Ordering information is given on any current masthead page.

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(35) Since the submission of this paper for publication, a paper has appeared which is concerned with the Al NMR study of dilute CH_3CN solutions of $AlCl_3$, $AlBr_3$, and AlI_3.[36] Chemical shift values are consistent with our data, if we take into account a constant difference of 1.2 ppm. In the 1 M concentration range, their spectrum is quite similar to that which we have obtained with $R = 19.7$. At lower concentrations, their spectra exhibit some features which are at the same positions and look like the bands that we have found to correspond to hydrated species.[24] Nevertheless, their assignment of the sharp line at −7.5 ppm to the *cis*-$AlCl_3(CH_3CN)_3$ complex is unambiguous, and this result provides an accuate basis for the calculation of the pairwise parameters, without any assumption regarding the stereochemistry of the C cation. The modified δ parameters are $\delta_{NN} = -2.83$, $\delta_{NCL} = -0.33$ and $\delta_{ClCl} = 0.59$. This basis leads to the calculated chemical shifts of 33.96 ppm for $Al(CH_3CN)_6^{3+}$, −23.96 ppm for $AlCl(CH_3CN)_5^{2+}$ −16.33 ppm for *cis*-$AlCl_2(CH_3CN)_4^+$, and −13.96 ppm for *trans*-$AlCl_2(CH_3CN)_4^+$ and to the assignment of our C band to the *trans*-$AlCl_2(CH_3CN)_4^+$ cation.

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Contribution from the Todd Wehr Chemistry Building,
Marquette University, Milwaukee, Wisconsin 53233

Infrared and Resonance Raman Spectra of Molecular Oxygen Adducts of [*N*,*N'*-Ethylenebis(acetylacetoniminato)]cobalt(II)

MAREK W. URBAN, YASUOMI NONAKA, and KAZUO NAKAMOTO*

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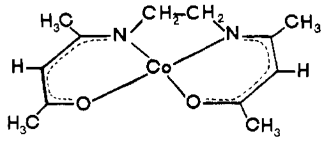
The infrared spectra of base-free $Co(acacen)O_2$ (acacen = *N*,*N'*-ethylenebis(acetylacetoniminato) anion) were measured with matrix cocondensation techniques. Its O_2 stretching frequency, $\nu(O_2)$ (1146 cm^{-1}), is much lower than that of previously reported $Co(TPP)O_2$ (1278 cm^{-1}). This low-frequency shift is interpreted as indicating that the negative charge on O_2 increases markedly in going from $Co(TPP)O_2$ to $Co(acacen)O_2$. The resonance Raman spectra of the O_2 adducts of Co(acacen) were measured in CH_2Cl_2 containing a variety of base ligands at low temperatures. Both axial (base) and in-plane ligand effects on $\nu(O_2)$ are noted: $Co(acacen)O_2$ (1146 cm^{-1}) vs. $Co(acacen)(1\text{-MeIm})O_2$ (1017 cm^{-1}) and $Co(TPP)(1\text{-MeIm})O_2$ (1142 cm^{-1}) vs. $Co(acacen)(1\text{-MeIm})O_2$ (1017 cm^{-1}). The $\nu(O_2)$ decreases linearly as the base strength of the axial ligand (B) increases in the $[Co(acacen)B]_2O_2$ series. Two different straight-line relationships were obtained, one for pure σ-donor ligands and one for σ- as well as π-donor ligands.

Introduction

Previously, we[1] prepared the "base-free" $Co(TPP)O_2$ (TPP = tetraphenylporphyrinato anion) via a matrix cocondensation reaction and located its O_2 stretching frequency ($\nu(O_2)$) at 1278 cm^{-1}, which is much higher than that of "superoxo" adducts (1195–1130 cm^{-1}).[2] For example, this frequency is higher by 136 cm^{-1} than that of $Co(TPP)(1\text{-MeIm})O_2$ (1-MeIm = 1-methylimidazole) (1142 cm^{-1}).[3] We attributed this large shift of $\nu(O_2)$ to the effect of the base ligand (1-MeIm) which tends to increase the negative charge on the O_2 via σ and π donation. A similar base ligand effect was noted for $[Co(salen)]_2O_2$ (1011 cm^{-1})[4] vs. $[Co(salen)(py)]_2O_2$ (888 cm^{-1})[5] (salen = *N*,*N'*-ethylenebis(salicylideniminato) anion).

In the present investigation, we focused our attention on the in-plane (chelating) ligand effect on $\nu(O_2)$. A previous investigation[6] of cobalt(II) Schiff base complexes studied the axial (base) and in-plane ligand effects by measuring equilibrium constants for oxygen adduct formation and redox potentials. One observation made was that the formation constant (K_{O_2} (mm^{-1})) for the reaction $Co(chelate)(py) + O_2 \rightleftharpoons Co(chelate)(py)O_2$ was much larger for Co(acacen)(py) (−0.28) than for Co(*p*-MeO(TPP))(py) (−3.1) (acacen = *N*,*N'*-ethylenebis(acetylacetoniminato) anion; *p*-MeO(TPP) = tetrakis(*p*-methoxyphenyl)porphyrinato anion). Also, the potential (volt vs. SCE) for the anodic wave Co(II) → Co(III) was much higher for the former (−0.59) than for the latter (−0.23).



These results were interpreted as indicating that, relative to acacen, *p*-MeO(TPP) delocalizes more electron density from

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