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Spectroscopic Characterization of the Complexes Formed in Acetonitrile Solutions of Aluminum Tribromide

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The $\text{AlBr}_3\text{-CH}_3\text{CN}$ system has been investigated by infrared, Raman, and Br and Al NMR spectroscopy in the range of the molar ratio $[\text{CH}_3\text{CN}]/[\text{AlBr}_3]$ of 4.7-64. The system consists exclusively of ionic complexes that share the only anion AlBr_4^- . Three octahedral cations have been characterized as $\text{Al}(\text{CH}_3\text{CN})_6^{3+}$, $\text{AlBr}(\text{CH}_3\text{CN})_5^{2+}$, and $\text{AlBr}_2(\text{CH}_3\text{CN})_4^+$, the last being likely to adopt the cis geometry because of pairwise interactions. The identification of the cations has been performed from their individual ionic charge. The method of evaluation is based on the comparison, for each concentration, of the experimental average ionic charge of the cations with the value that can be calculated from a quantitative curve analysis of the spectra.

Introduction

The chemical structure of complexes formed by aluminum halides in solution in organic Lewis bases is still often an open question despite the fact that it has been the object of several investigations.² This problem arises undoubtedly from the very large variety of bonding situations that the aluminum atom can adopt: it may be found in coordination states III, IV, V, and VI.³ Furthermore, the aluminum halides, when dissolved in an organic solvent L, may form either molecular adducts ($\text{AlX}_3 \cdot n\text{L}$) or ionic complexes so that several species may exist simultaneously, according to temperature and concentration conditions. Because of this chemical flexibility, it is difficult to predict the structure of the complexes from tabulated data such as donicity factors⁴ or donor parameters.⁵ Consequently, we believe that the spectroscopic analysis of binary mixtures of aluminum halides with some organic bases is of valuable interest.

In the case of tetrahydrofuran (which has a low dielectric constant of 7.8⁶), we have found that the species formed with AlCl_3 and AlBr_3 are mainly molecular;⁷ this result accounts for the weak electrical conductivity of this system.⁸ On the other hand, the electrical conductivity of solutions of AlCl_3 in CH_3CN is greater and indicates a more important ionic dissociation, as expected from the higher value of the dielectric constant, 38.8.⁴ However, the nature of the ionic species is far from being unambiguously established.⁹⁻¹² Preliminary experiments by infrared and ²⁷Al nuclear magnetic resonance spectroscopy have shown that the structural analysis of solutions of AlCl_3 or AlBr_3 in CH_3CN is feasible and is of great chemical interest since equilibrium reactions occur between several ionic species.¹³ Unfortunately the limited accuracy of instruments available at that time restricted these studies so that only incomplete assignments were made. Now, with

modern FT IR and NMR spectrometers of considerably improved performances, it is worthwhile to reexamine such solutions. The aim of this paper is to report on our recent spectroscopic results concerning solutions of AlBr_3 in acetonitrile over a large range of concentration (0.2-4 M).

Experimental Section

Solution Preparation. Aluminum bromide and acetonitrile were purified as previously described.¹⁴ Aluminum bromide was dissolved in acetonitrile at low temperatures with use of conventional vacuum techniques. The composition of each solution is given by the molar ratio $R = [\text{CH}_3\text{CN}]/[\text{AlBr}_3]$.

NMR Spectra. The ²⁷Al NMR spectra were recorded on a WH 90C Bruker instrument equipped with a multinuclei probe and a Fourier transform device. The resonance frequency was 23.45 MHz. Samples were sealed in 8-mm external diameter tubes, which were inserted inside a classical 10-mm tube containing a small amount of D_2O for lock purposes. The reference was $\text{Al}(\text{H}_2\text{O})_6^{3+}$, whose spectrum was recorded under the same conditions. All spectra were recorded at 26 °C, and the chemical shifts are reported according to the usual convention.¹⁵

The fact that the system displays both narrow and broad lines has led to some difficulties in the measurements of intensities. The best results were obtained according to the following procedure. We used a large sweep width of 12 000 Hz, which allows a rapid acquisition of the decay and leads to a greater number of significant points, which were necessary to obtain a satisfactory definition of the broad bands. But, in addition, we wanted to measure accurately the intensity of the sharp lines; consequently it was necessary to allow the spin system to return to its thermal equilibrium between each scan. For this purpose, we used a waiting time of 30 s after each acquisition. An exponential filtering of 2 Hz was used, and the spectra were recorded on a normal width of 4800 Hz. Any other different procedure led to irreproducible intensities. The intensity measurements given in this paper are the mean value of at least three integrations. For purposes of assignment, the NMR spectra have been analyzed by a least-squares method. A simulated spectrum was produced from a combination of Lorentzian curves and compared to the experimental profile. The parameters of each curve were simultaneously adjusted by a perturbation program in order to reach the best fit between experimental and calculated spectra.

NMR spectra of ⁸¹Br were recorded on the same instrument at 24.31 MHz.

Vibrational Spectra. The Raman spectra were recorded on a Coderg T800 spectrometer powered by a Spectra-Physics Ar⁺ laser tuned at 488.0 nm. The spectral slit width was approximately 3 cm^{-1} , and the spectra were obtained with a rotating cell, which was filled in a drybox.

In infrared, we have observed the very easy occurrence of chemical reactions between the solutions and the optical windows or metal parts of the standard IR cell or of the syringe. The only way to avoid this difficulty was to use a specially designed polyethylene cell. This cell was flushed with dry argon, and the solution to be analyzed was

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Table I. Spectroscopic Data Related to Identified Ionic Species in CH₃CN Solutions of AlBr₃

	Al(CH ₃ CN) ₆ ³⁺ A	AlBr(CH ₃ CN) ₅ ²⁺ B	AlBr ₂ (CH ₃ CN) ₄ ⁺ C	AlBr ₄ ⁻
Stoichiometry ^a	3/2	5/3	2	
IR, cm ⁻¹	478 (8) ^b	450 (10) ^b	433	403
Raman, cm ⁻¹	212
δ	-34	-31	-23	80
Δν _{1/2} , Hz	25	80	60	16

^a [CH₃CN]/[AlBr₃] in neutral complex; see text. ^b Isotopic shift (ν_H - ν_D) for the perdeuterated species.

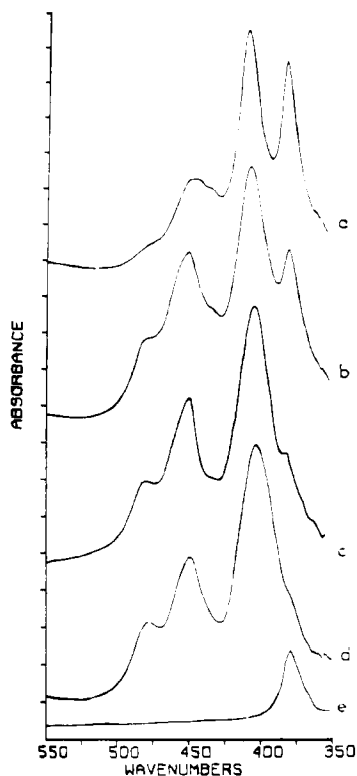


Figure 1. Effect of concentration on the IR spectra of aluminum bromide in acetonitrile: (a) $R = [\text{CH}_3\text{CN}]/[\text{AlBr}_3] = 82$; (b) $R = 28.6$; (c) $R = 9.5$; (d) $R = 6.9$; (e) pure CH₃CN.

transferred directly from the reaction vessel to the cell by using silicone and polytetrafluoroethylene tubing and a peristaltic pump.

The infrared spectra were recorded from 350 to 4000 cm⁻¹ with a Nicolet MX-1 Fourier transform interferometer. The energy level at the detector was very low because of the very important absorption of the polyethylene windows (thickness 0.6 mm each), and despite the very high sensitivity of the instrument, approximately 3000 scans were necessary to obtain an accurate 2-cm⁻¹ resolution spectrum with a satisfactory S/N ratio. Three narrow-frequency intervals (3050–2700, 1500–1350, and 750–700 cm⁻¹) were obscured by the strongest absorption bands of the PE windows, which prevent the system from computing the difference between single-beam spectra. In other frequency regions, we have checked the two following points: (i) that the compensation of polyethylene bands was accurate and reproducible and (ii) that the spectrum of a polystyrene reference film remained strictly identical when recorded with or without the PE cell in the beam.

Results and Discussion

Vibrational Spectra. The Raman spectra of solutions of AlBr₃ in acetonitrile were quite difficult to obtain, and we have observed only the expected band for free CH₃CN near 380 cm⁻¹ and a narrow intense and polarized line at 212 cm⁻¹. Some IR bands due to bound CH₃CN are detected above 600 cm⁻¹. They are consistent with our previous results related to solid compounds,¹⁴ but they do not allow a detailed discussion of the structure of dissolved complex species. All the infrared spectra show a strong feature near 450 cm⁻¹ and a

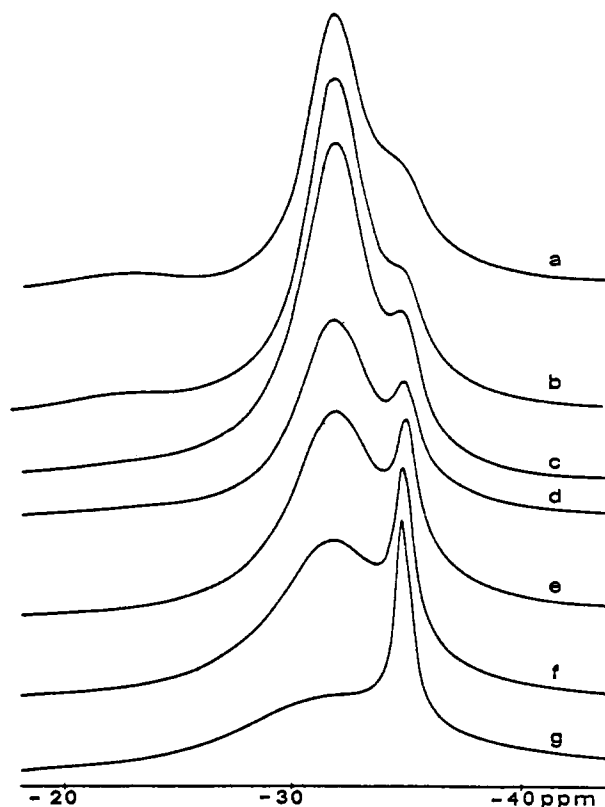


Figure 2. Concentration dependence of the Al magnetic resonance spectra of aluminum tribromide in acetonitrile. The resonances are upfield from the external standard Al(H₂O)₆³⁺, and $R = [\text{CH}_3\text{CN}]/[\text{AlBr}_3]$. R values for the spectra are as follows: (a) 64.7; (b) 34.9; (c) 18.8; (d) 11.1; (e) 9.1; (f) 6.7; (g) 4.7.

very intense band at about 400 cm⁻¹ (Figure 1). Concentrated solutions yield an additional band at 478 cm⁻¹ while a weak absorption at 433 cm⁻¹ is observed with the solution corresponding to $R = [\text{CH}_3\text{CN}]/[\text{AlBr}_3] = 82$. The band located at 383 cm⁻¹ arises from free CH₃CN. The infrared spectrum of AlBr₃ dissolved in CD₃CN ($R = 9.2$) exhibits three bands at 470, 440, and 403 cm⁻¹ due to complex species.

The infrared band at 403 cm⁻¹ and the polarized Raman line at 212 cm⁻¹ are well-known features of the AlBr₄⁻ anion.^{16,17} Other observed infrared bands below 600 cm⁻¹ are difficult to assign; nevertheless the comparison with the data related to solid compounds^{14,17} suggests that the absorptions observed at 478 and 450 cm⁻¹ may be due to the strongest bands of the cations Al(CH₃CN)₆³⁺ and AlBr(CH₃CN)₅²⁺, respectively (Table I). The observed isotopic shifts of IR frequencies for solutions in CD₃CN are consistent with these assignments. Furthermore, the lack of a Raman line near 198 cm⁻¹ indicates that no appreciable amount of the Al₂Br₇⁻ anion

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is formed under our experimental conditions.¹⁸

NMR Spectra. Each ^{27}Al NMR spectrum of CH_3CN solutions of AlBr_3 ($4.7 \leq R \leq 64$) displays a very sharp and intense line ($\Delta\nu_{1/2} = 16$ Hz) at +80.0 ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ taken as an external reference and a multiline resonance signal at about -30 ppm. Figure 2 presents the concentration dependence of the spectra. Each spectrum shows an intense peak at -31 ppm. When the dilution ratio R is low (greater concentrations of AlBr_3), a second narrow line is observed at -34 ppm. When the dilution is increased, the latter decreases regularly while a new band appears at -23 ppm for the upper value of R .

These spectra look quite different from those previously described in the literature.^{10,11} We feel that the high performances of our instrument, particularly because of the lock device, result in an increased S/N ratio, a better accuracy in quantitative measurements (see below), and a very good consistency within a series of solutions of various concentrations.

Before going through a quantitative analysis of our results, we had to establish, at first, that we were dealing with all the aluminum nuclei present in the solutions and, second, that quantitative measurements were feasible under our experimental conditions. This step was necessary because very broad lines might not be observed and would escape quantitative analysis under our experimental conditions. For these purposes we have made the following experiments: one of the solutions to be analyzed and a titrated reference solution of the cation $\text{Al}(\text{D}_2\text{O})_6^{3+}$ were separately placed in concentric tubes of calibrated diameters. The ^{27}Al NMR spectra were recorded under the same conditions as above, and the bands were integrated as previously. Within the experimental uncertainty, a few percent, the concentration of aluminum found by NMR in the CH_3CN solution was identical to that calculated from the sample preparation. Thus, we concluded that most Al nuclei were detected and that quantitative measurements were correct. Furthermore this result showed unambiguously that the relatively narrow bands are not superimposed on a broad one. Such a broad band would occur from species containing asymmetrical Al sites with short relaxation times arising from a quadrupolar mechanism.

In addition, attempts to detect the presence of the bromide anions by means of ^{81}Br NMR always failed in the case of CH_3CN solutions of AlBr_3 , whereas this is easily performed with a dilute solution of LiBr in CH_3CN . We conclude that Br^- anions are not significantly formed in our solutions of AlBr_3 .

According to the literature data,¹⁹ we assign the sharp line at +80 ppm to the AlBr_4^- anion; this result is consistent with the above vibrational analysis. The concentration dependence of the NMR spectrum (Figure 2) shows that at least three aluminum species are responsible for the resonances observed at about -30 ppm. On the other hand, such values of the chemical shifts¹⁹ suggest that we are dealing with octahedrally coordinated Al atoms as a part of ionic complexes $[\text{qAlBr}_4(\text{AlBr}_{3-\text{q}}(\text{CH}_3\text{CN})_{3+\text{q}})^{\text{q}+}]$. Thus, the knowledge of the ionic charge q of these species should be sufficient to establish the number of bound Br atoms and then the ionic structure and the stoichiometry of the corresponding complexes. We have derived a method to evaluate the individual ionic charge of each octahedral species according to the following procedure. Keeping in mind that AlBr_4^- species is the only anion and that negative and positive ionic charges must be balanced, the above ionic formula shows that the weighed average value \bar{q} for the ionic charge of the octahedral species

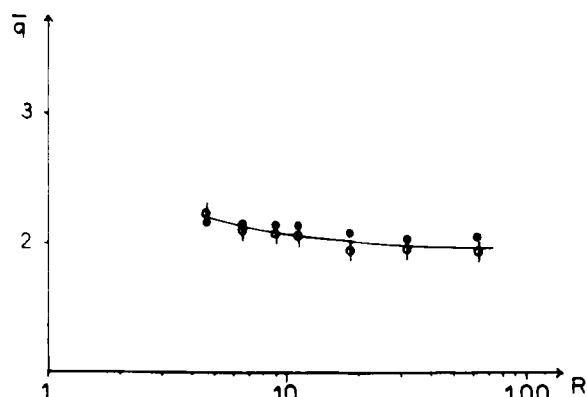


Figure 3. Plot of the average ionic charge (\bar{q}) vs. molar ratios R : \diamond , experimental average charge obtained from integration (and uncertainty); \bullet , calculated average charge from simulated spectra.

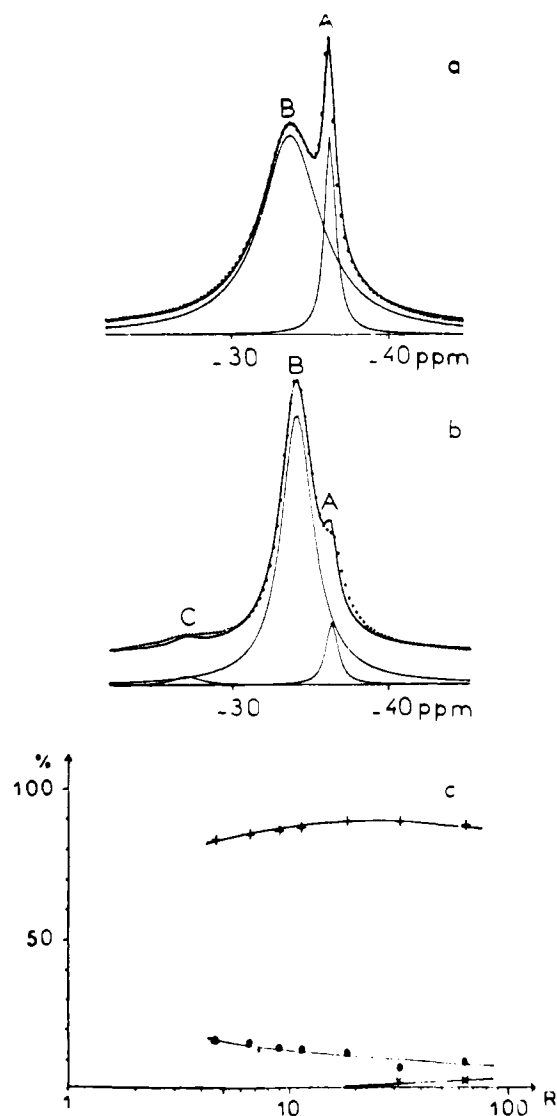


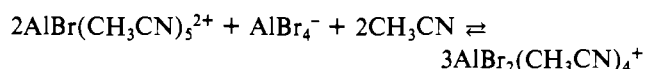
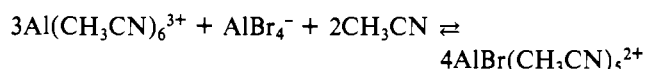
Figure 4. Experimental and simulated ^{27}Al NMR spectra (see Experimental Section): (a) $R = 6.7$; (b) $R = 34.9$ (\diamond , experimental spectrum; —, simulated spectrum with A, B, and C Lorentzians). Plot c is percentage of each octahedral species vs. molar ratios R (\bullet , +, and \times are for A, B, and C octahedral species, respectively).

may be experimentally evaluated by measuring the ratio of the area of the AlBr_4^- peak to the total area of the signals near -30 ppm. The value of this ratio decreases from 2.25 to 1.94 when R increases (Figure 3). On the other hand, the curve analysis of the resonance signal arising from octahedral species

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(Figure 4a,b) confirms the existence of three species A, B, and C (see Table I) and leads to their relative concentrations (Figure 4c). From these results, we can calculate an average ionic charge \bar{q} for each R value if we a priori assign a charge q to each species (A, B, or C). A good agreement between experimental and calculated average charges is only obtained with the set $q_A = 3+$, $q_B = 2+$, and $q_C = 1+$ (Figure 3). The stoichiometry of a particular ionic complex $[(\text{AlBr}_{3-q}(\text{CH}_3\text{CN})_{3+q})^{q+}, q\text{AlBr}_4^-]$ is given by $n = (\text{CH}_3\text{CN})/(\text{AlBr}_3) = (3+q)/(1+q)$ and thus $n_A = 3/2$, $n_B = 5/3$, and $n_C = 2$ if n_A , n_B , and n_C stand for the stoichiometries of the neutral complexes containing A, B, and C cations, respectively. The relative concentrations $[C]/[B]$ and $[B]/[A]$ are found to increase when the concentration of AlBr_3 decreases; this fact is consistent with the order of stoichiometries $n_C > n_B > n_A$. Thus, the above assumption of octahedral coordination is corroborated. Finally our results may be summarized by the two solvolysis reactions



These conclusions confirm the interpretation of the above infrared data; the remaining unassigned infrared band at 433 cm^{-1} observed in dilute solutions corresponds to a stretching mode $\nu(\text{Al-N})$ or $\nu(\text{Al-Br})$ of the $\text{AlBr}_2(\text{CH}_3\text{CN})_4^+$ cation.

The last structural property that can be discussed on the basis of the above results concerns the stereoisomerism of the $\text{AlBr}_2(\text{CH}_3\text{CN})_4^+$ cation. The symmetry of this cation may be deduced from the NMR data by using a procedure similar to the one used for the octahedral complexes $[\text{NbCl}_n\text{Br}_{5-n}(\text{CH}_3\text{CN})]^{20}$. The chemical shifts of species A, B, and C do not vary linearly according to the number of bromine atoms bound to aluminum. Thus, as previously stated in the case of tetrahaloaluminate anions $\text{AlCl}_{4-n}\text{Br}_n^-$,²¹ the pairwise additivity increment model is the more convenient to account for this result. The chemical shifts may be derived in terms of three pairwise parameters:

$$\begin{aligned} \delta_C(\text{trans}) &= 4\delta_{\text{NN}} + 8\delta_{\text{NBr}} \\ \delta_C(\text{cis}) &= 5\delta_{\text{NN}} + 6\delta_{\text{NBr}} + \delta_{\text{BrBr}} \quad \delta_B = 8\delta_{\text{NN}} + 4\delta_{\text{NBr}} \\ \delta_A &= 12\delta_{\text{NN}} \end{aligned}$$

These relations indicate that the trans geometry would lead to equal values for the differences $\delta_C - \delta_B$ and $\delta_B - \delta_A$. Consequently, only the cis geometry agrees with the observed

chemical shifts. Then the following pairwise parameters are $\delta_{\text{NN}} = -2.83\text{ ppm}$, $\delta_{\text{NBr}} = -2.09\text{ ppm}$, and $\delta_{\text{BrBr}} = 3.69\text{ ppm}$.

This tendency for the cis geometry may be explained by using the VSEPR model of Gillespie^{5,22} or the stereochemical model derived by Zahrobsky,²³ which are based upon non-bonded interactions. According to the latter, the preferred geometry is that which corresponds to the minimum steric hindrance in each of the three planes of an octahedral framework. In each plane, the steric hindrance is evaluated from the sum of the so-called steric angles, which are assumed to be equal to the trace of the solid angle occupied by each ligand. The cis geometry is preferred when the steric angle is not too large. If this steric angle is significantly larger than that corresponding to the van der Waals radius of the donor atom, the more stable geometry is the trans model. Thus the AlX_2L_4^+ cation corresponds to the cis geometry in the case of a sharp-pointed ligand such as CH_3CN and to the trans arrangement with $\text{C}_4\text{H}_8\text{O}$ and $\text{C}_5\text{H}_5\text{N}$, which are more bulky.^{24,25}

Conclusion

The conjunction of two techniques, vibrational spectroscopy and nuclear magnetic resonance of the Al and Br nuclei, enables the investigation of solutions of AlBr_3 in acetonitrile without any assumption. All likely chemical reactions were considered, and the eventual resulting species have been investigated by means of the appropriate spectroscopic method. No molecular adducts have been identified so that AlBr_3 is entirely dissociated into ions when dissolved in CH_3CN at 0.2–4 M concentrations. The only anion formed is AlBr_4^- , and three cations have been characterized. However no counterpart for the 1:1 solid compound¹⁴ has been detected. Among the three cations, two of them, namely, $\text{Al}(\text{CH}_3\text{CN})_6^{3+}$ and $\text{AlBr}(\text{CH}_3\text{CN})_5^{2+}$, are identical with those identified in the crystallized compounds $2\text{AlBr}_3 \cdot 3\text{CH}_3\text{CN}$ ¹⁴ and $3\text{AlBr}_3 \cdot 5\text{CH}_3\text{CN}$,¹⁷ respectively. The third cation, $\text{AlBr}_2(\text{CH}_3\text{CN})_4^+$, has no equivalent in solid phases; the stoichiometry of the corresponding neutral compound is $\text{AlBr}_3 \cdot 2\text{CH}_3\text{CN}$, but its ionic structure differs from that of the isolated 1:2 solid complex, which is $[2\text{AlBr}_4^-, \text{AlBr}(\text{CH}_3\text{CN})_5^{2+} \cdot \text{CH}_3\text{CN}]$.¹⁷

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Registry No. AlBr_3 , 7727-15-3; $\text{Al}(\text{CH}_3\text{CN})_6^{3+}$, 25159-95-9; $\text{AlBr}(\text{CH}_3\text{CN})_5^{2+}$, 62389-67-7; $\text{AlBr}_2(\text{CH}_3\text{CN})_4^+$, 62389-68-8; AlBr_4^- , 22602-42-2.

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