Vibrational Spectra and Force Constants of the Tetrachloroaluminate, Tetrabromoaluminate, and mixed Bromochloroaluminate Ions

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The i.r. and Raman spectra of the five ions $[AlCl_nBr_{4-n}]^-$ ($0 \leqslant n \leqslant 4$), which form an equilibrated mixture in solution have been determined and fitted to a unified Urey–Bradley force field.

VIBRATIONAL spectra have been obtained for several series of tetrahalogenometallate ions $[MX_nY_{4-n}]^{m-}$ ($0 \leqslant n \leqslant 4$; X,Y = Cl, Br, or I; M = Fe,[1] Tl,[2] or Zn [3]) and partial assignments have been discussed. In the case of the corresponding series of tetrahalogeno-aluminates spectra of only the terminal ions of the series, $AlCl_4^-$ (refs. 4—6) and $AlBr_4^-$ (refs. 7 and 8) have been reported.

The existence of the mixed ions $[AlCl_nBr_{4-n}]^-$ ($n = 1$—3) has been shown [9] by use of ^{27}Al n.m.r. spectroscopy; peaks due to all five ions were observed in solutions of aluminium bromide and tetra-(n-propyl)-bromide in dichloromethane. In solutions whose alkyl-ammonium bromide to aluminium bromide ratio was $<1 : 1$ there was a single broad ^{27}Al signal indicative of rapid exchange between the ions. Compounds of the mixed ions, whose vibrational spectra have not hitherto been reported, were not isolated.

In the present study, we have found that salts of composition $[NMe_4]^+[AlCl_xBr_{4-x}]^-$ ($0 \leqslant x \leqslant 4$) can be obtained only as mixtures containing all five ions; exchange in solution occurs too rapidly for compounds of individual chlorobromoaluminate ions to be isolated. Exchange may not occur in the solid, as mechanical mixtures from compositions of different values of x did not equilibrate. I.r. and Raman spectra of such mixtures, with overall compositions ranging from x 3·0—0·96 were obtained, and showed bands due to all five ions. Bands due to $[AlCl_4]^-$ and $[AlBr_4]^-$ were readily identified from their known positions in spectra of the pure tetramethylammonium salts, and several other bands in the spectra of the ionic mixtures were un-ambiguously assigned to individual ions on the basis of their intensity variation with changing values of x. In principle, once one band has been assigned to an in-dividual ion, other bands due to that ion should be identifiable by their constant intensity-ratio to the assigned band throughout the whole range of halogen ratios. In practice, it was not possible to assign many bands in the i.r. or Raman spectra on this principle. We therefore performed a normal-co-ordinate calculation for the five ions, assuming a Urey–Bradley Force Field (UBFF) and force constants transferable between the

ions. This procedure gave satisfactory results for the predominantly stretching modes of the ions, but bending modes were less successfully defined.

EXPERIMENTAL

Purification of Reagents.—Anhydrous aluminium halides were purified by repeated vacuum sublimation, the bromide alone but the chloride from an admixture with a few % of aluminium powder and sodium chloride. Tetramethyl-ammonium halides (reagent grade) were vacuum dried (P_2O_5). Acetonitrile and nitromethane were set aside over phosphorus pentoxide for 24 h, then decanted and distilled in a current of dry nitrogen with rejection of the first and last quarters. Reagent-grade toluene was dried over sodium.

Preparation of Samples.—Since all the tetrahalogeno-aluminates are water sensitive, dry-box and vacuum-line techniques were employed for all sample preparation and handling.

Tetramethylammonium tetrachloroaluminate was obtained by dissolving aluminium chloride (*ca.* 2·0 g) in dry aceto-nitrile (5—10 ml), followed by tetramethylammonium chloride (1·0—1·05 mol equiv.). The solution was filtered (to remove *e.g.* excess of tetramethylammonium salt, also traces of water in the reagents leave a slight gelatinous precipitate) and evaporated to small bulk. Crystals were obtained by addition of toluene and were washed with toluene and vacuum-dried to give *tetramethylammonium tetrachloroaluminate*, m.p. 300° (decomp.) (Found: C, 19·3; H, 5·2; N, 5·7. $C_4H_{12}AlCl_4N$ requires C, 19·7; H, 5·0; N, 5·8%).

An analogous procedure for the respective bromides gave *tetramethylammonium tetrabromoaluminate*, m.p. 270° (de-comp.) (Found: C, 11·4; H, 2·9; N, 3·3. $C_4H_{12}AlBr_4N$ requires C, 11·4; H, 2·9; N, 3·3%).

Mixtures of various Cl : Br ratios were obtained by dissolving different proportions of these compounds in acetonitrile and evaporating the solutions to dryness, and also by treating as before, aluminium chloride with tetra-methylammonium bromide and aluminium bromide with tetramethylammonium chloride. The halogen ratios of these mixtures, determined by analysis and expressed as values of x in the general formula $[NMe_4]^+[AlCl_xBr_{4-x}]^-$, are given in Table 1.

Raman Spectroscopy.—Samples of the tetramethyl-ammonium salts were sealed into capillary tubes (1×50 mm) with one end ground flat, and their Raman spectra

[1] C. A. Clausen and M. L. Good, *Inorg. Chem.*, 1970, **9**, 220.
[2] R. W. Matthews and R. A. Walton, *J. Chem. Soc. (A)*, 1968, 1639.
[3] G. B. Deacon, J. H. S. Green, and F. B. Taylor, *Austral. J. Chem.*, 1967, **20**, 2069.
[4] D. E. H. Jones and J. L. Wood, *Spectrochim. Acta*, 1967, **23A**, 2695.
[5] G. L. Carlson, *Spectrochim. Acta*, 1963, **19**, 1293; C. Souris-seau and B. Pasquier, *Spectrochim. Acta*, 1970, **26A**, 1279.

[6] G. Torsi, G. Mamantov, and G. M. Begun, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 553.
[7] E. Kinsella and J. Coward, *Spectrochim. Acta*, 1968, **24A**, 2139.
[8] D. H. Brown and D. T. Stewart, *Spectrochim. Acta*, 1970, **26A**, 344.
[9] R. G. Kidd and D. R. Truax, *J. Amer. Chem. Soc.*, 1968, **90**, 6867.

were examined on a Cary 81 photoelectric instrument with helium–neon laser excitation. A mechanical mixture in 1 : 1 molar ratio of the samples with $x = 3\cdot0$ and $x = 0\cdot96$ was also examined to provide an otherwise unobtainable set of ionic ratios (scrambling between individual crystals of the two components did not occur, judging from the difference between the spectra of this sample and the fully equilibrated one with $x = 2\cdot0$). Pure tetramethylammonium tetrachloroaluminate and tetrabromoaluminate were also examined, as were solutions of the salts and mixtures in acetonitrile and nitromethane. Tetramethylammonium chloride and bromide were examined as crystalline material (they are scarcely soluble in acetonitrile or nitromethane) to verify attributions to the NMe_4^+ ion.

I.r. Spectroscopy.—Samples of the salts were examined as Nujol mulls, solutions in acetonitrile and nitromethane, and as dispersions in Polythene, by use of Perkin-Elmer 257 and Grubb–Parsons Spectromaster and DM 4 instruments, and a far-i.r. interferometer constructed in the Chemistry Department of the University of Manchester. The mulls and solutions were contained in sealed Polythene cells to avoid the possibility of halogen exchange with alkali metal halide windows.[10]

$[AlCl_4]^-$ or a chlorine atom into $[AlBr_4]^-$ reduces the symmetry to C_{3v} and changes the vibrational representation to $3a_1(i,R) + 3e(i,R)$. A further such substitution gives $[AlCl_2Br_2]^-$ of C_{2v} symmetry and representation $4a_1(i,R) + a_2(R) + 2b_1(i,R) + 2b_2(i,R)$.

In the Raman and i.r. spectra of the tetramethylammonium salts of these ions, a number of common bands can be assigned to the NMe_4^+ cation, at 948, 752, 457, 388, 365, and 200 cm^{-1}, though small deviations occur from these mean positions in individual solid specimens. Pure tetramethylammonium halides proved very poor Raman scatterers, but all these bands were observed in the Raman spectrum of solid tetramethylammonium bromide, and the strongest ones (948 and 752 cm^{-1}) in that of the chloride as well. The fundamental frequencies of the $[AlCl_nBr_{4-n}]^-$ ions all lie <600 cm^{-1}, since the highest-frequency modes will be those of $[AlCl_4]^-$ whose highest fundamental occurs at 495 cm^{-1}. Table 1 lists the observed i.r. and Raman bands in the spectra of the pure tetramethylammonium tetrahalogenoaluminates and the equilibrium mixtures.

TABLE 1

I.r. and Raman intensities (cm^{-1}) of bands in $[NMe_4]^+[AlCl_xBr_{4-x}]^-$ mixtures

Band	4·0 I.r.	4·0 R	3·0 I.r.	3·0 R	2·0 I.r.	2·0 R	0·96 + 3·0 I.r.	0·96 + 3·0 R	0·96 I.r.	0·96 R	0 I.r.	0 R	Assignment
752	s	100	s	100	s	100		100	s	100	s	100	$[NMe_4]^+$ Reference band for Raman intensities
495	vsb		sb		sb				m				} $[AlCl_4]^-$
488		11		12		11		11		9			}
465			m		vs				m				$[AlCl_2Br_2]^-$
440				6		15		7					$[AlCl_3Br]^-$
425										11		19	$[AlBr_4]^-$
418			wsh		wsh								$[AlCl_2Br_2]^-$?
404			mb		vsb				vsb		vsb		} $[AlBr_4]^-$
400						16		12		21		33	}
352		150		80		21		67		3			$[AlCl_4]^-$
308				115		80		87		19			} $[AlCl_3Br]^-$
304			s		s				w				}
278				63		140		67		74			} $[AlCl_2Br_2]^-$
272			m		m				w				}
247				15		120		62		210			} $[AlClBr_3]^-$
241					wb				wb				}
214			mb*	35		47			m*	206		720	$[AlBr_4]^-$
183		54		25									$[AlCl_4]^-$
180					m								$[AlCl_3Br]^-$?
168					m								$[AlCl_3Br]^-$?
156					m								$[AlCl_3Br]^-$?
144					m				vb				$[AlCl_2Br_2]^-$? or $[AlClBr_3]^-$?
134										350b			} $[AlClBr_3]^-$?
129									w				}
125		150b		200b		250b		170b					$[AlCl_4]^-$, $[AlCl_2Br_2]^-$?
119								130	m	220	m	290	$[AlBr_4]^-$
76											w	78	$[AlBr_4]^-$

* Solid phases only. s = Strong, v = very, m = medium, w = weak, b = broad, sh = shoulder.

RESULTS AND DISCUSSION

The $[AlCl_4]^-$ ion has been shown by X-ray crystallography to have tetrahedral symmetry,[11] and it is reasonable to assume the same geometry for $[AlBr_4]^-$. The normal modes of these ions will therefore be given by $a_1(R) + e(R) + 2f_2(i,R)$ (i denotes infrared and R Raman activity). Substitution of a bromine atom into

10 D. E. H. Jones and J. L. Wood, *J. Chem. Soc. (A)*, 1966, 1448.
11 N. C. Baenziger, *Acta Cryst.*, 1951, **4**, 216.

Spectra of $[AlCl_4]^-$ *and* $[AlBr_4]^-$.—The three frequencies 495, 352, and 180 cm^{-1} are in agreement with the previously published assignments[4-6] for $AlCl_4^-$. However, there is some uncertainty regarding the lowest fundamental of this ion, which has been reported to be at 145 cm^{-1} (ref. 5) and at 121 cm^{-1} (ref. 6). Our Raman spectra of $[NMe_4]^+[AlCl_4]^-$ (Table 1) show a shoulder on the exciting line at 125 cm^{-1} and no band at 145 cm^{-1}.

A similar uncertainty exists for $[AlBr_4]^-$. We agree

with Brown and Stewart [8] that the three higher fundamentals are at 400, 213, and 117 cm⁻¹. However, they report ν_2 of this ion at 98 cm⁻¹, a band which we do not observe. Our Raman spectra of crystalline $[\text{NMe}_4]^+[\text{AlBr}_4]^-$ show a clear band at 76 cm⁻¹ (Figure 1)
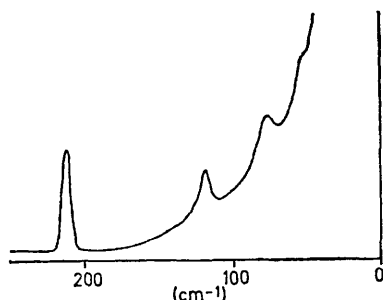

FIGURE 1 Low-frequency section of Raman spectrum of crystalline $[\text{NMe}_4]^+[\text{AlBr}_4]^-$, showing bands at 214, 117, and 76 cm⁻¹

which is still present, though weakly, in spectra of solutions in acetonitrile. This is therefore unlikely to be a lattice mode, and we tentatively ascribe it to the e mode ν_2. The a_1 mode for $[\text{AlBr}_4]^-$ should be i.r.-inactive; we observe an i.r. absorption assigned to this mode in some solid specimens and attribute it to crystal effects.

Spectra of $[\text{AlCl}_3\text{Br}]^-$, $[\text{AlCl}_2\text{Br}_2]^-$, and $[\text{AlClBr}_3]^-$.—Figure 2 shows schematically the strongest Raman bands for all the samples studied. In general, solution spectra were markedly less intense than those of the solid specimens, whose relative intensities are indicated in Figure 2. Only $[\text{NMe}_4]^+[\text{AlBr}_4]^-$ exhibited a useful Raman spectrum below 100 cm⁻¹; for the other specimens exciting-line scatter degraded the spectra below *ca.* 200 cm⁻¹ so that only strong bands could be discerned in this region. The band at 352 cm⁻¹ due to $[\text{AlCl}_4]^-$, and the one at 214 cm⁻¹ due to $[\text{AlBr}_4]^-$, are clearly apparent in all the spectra of the ionic mixtures, confirming the existence of an equilibrium between all the ions. It is obvious from their intensity variations with composition that the strong Raman bands at 308, 278, and 247 cm⁻¹ must be due to $[\text{AlCl}_3\text{Br}]^-$, $[\text{AlCl}_2\text{Br}_2]^-$, and $[\text{AlClBr}_3]^-$. Similarly, but with less certainty, the bands at 465 and 440 cm⁻¹ may be assigned to $[\text{AlCl}_2\text{Br}_2]^-$ and $[\text{AlCl}_3\text{Br}]^-$ respectively on the basis of their i.r. intensities. Further assignments of bands to particular ions could not be made with certainty, either because the bands were too weak or because their variation of intensity with composition suggested coincidence of bands from more than one ion. By carrying out a normal-co-ordinate calculation using the known vibrational frequencies of $[\text{AlCl}_4]^-$ and $[\text{AlBr}_4]^-$, and assuming transferability of force constants to the other ions it was hoped to obtain close estimates of the vibrational frequencies for the three mixed ions which would enable further assignments to be made.

Normal-mode Analysis.—The normal-co-ordinate calculations have been carried out by use of the UBFF, which has been applied successfully to many tetrahedral systems, and in particular to tetrahalogen species.[12,13] Shimanouchi has shown [14] that the vibrational frequencies of CY_nX_{4-n} (X = Cl, Y = F, Br, or I) may be closely approximated by a UBFF whose force constants have been transferred or interpolated from those of CX_4, CY_4, C_2X_4, and C_2Y_4. In the series of ions
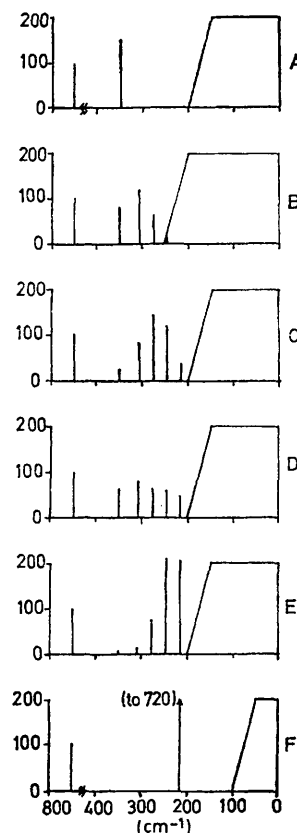

FIGURE 2 Schematic Raman spectra of solids of composition $[\text{NMe}_4]^+[\text{AlCl}_x\text{Br}_{4-x}]^-$ for various values of *x:* A, 4; B, 3·0; C, 2·0; D, a mechanical mixture of samples B and E; E, 0·96; and F, 0

Only the very strong bands at 352, 308, 278, 247, and 214 cm⁻¹ are represented, with intensities scaled relative to the NMe_4^+ band at 752 cm⁻¹ = 100. The trapezoidal regions at the right indicate the regions in which exciting-line scatter degrades the spectra

$[\text{AlCl}_n\text{Br}_{4-n}]^-$ all angles have been assumed tetrahedral, and bond lengths Al–Cl 2·13 (ref. 11) and Al–Br 2·29 Å (ref. 15) used throughout. The linear repulsion constant of the UBFF, F', was set equal to $-0·1F$ (the conventional approximation) and the intramolecular tension, K, expressed in terms of F.[12]

With these approximations the potential-energy expression for the $[\text{AlX}_4]^-$ ions contains only three force constants. Optimum values of these constants for $[\text{AlCl}_4]^-$ and $[\text{AlBr}_4]^-$ were obtained from the observed

[12] T. Shimanouchi, *J. Chem. Phys.*, 1949, **17**, 245.
[13] A. Miller and B. Krebs, *J. Mol. Spectroscopy*, 1967, **24**(2), 180 and 197.

[14] T. Shimanouchi, *Pure Appl. Chem.*, 1963, **7**(1), 131.
[15] *Chem. Soc. Special Publ.*, No. 11, 1958 and No. 18, 1965.

vibrational frequencies using a force-constant refinement program due to Schachtschneider.[16] Two fits were explored for [AlCl$_4$]$^-$ (Table 2). Assignment (1) uses our own values for ν_1, ν_3, and ν_4, but takes the value of ν_2 145 cm^{-1} from ref. 5; assignment (2) takes data from

TABLE 2

Calculated spectra (cm^{-1}) and corresponding force-constants (mdyne Å^{-1}) for [AlCl$_4$]$^-$ and [AlBr$_4$]$^-$, using a UBFF field

(a) Frequencies

| | [AlBr$_4$]$^-$ | | [AlCl$_4$]$^-$ | | | |
| | | | Assignment (1) | | Assignment (2) | |
Mode	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$\nu_1(a_1)$	214	214	349	349	351	351
$\nu_2(e)$	76	81	145	139	121	128
$\nu_3(f_2)$	405	405	495	495	490	494
$\nu_4(f_2)$	118	116	183	186	186	175

(b) Force constants

K	1·37		1·66	1·69
H	0·030		0·053	0·032
F	0·20		0·22	0·22

the more recent high-quality Raman spectra of ref. 6 for molten NaCl–AlCl$_3$ mixtures, which indicate strongly that ν_2 is 121 cm^{-1}. This is consistent with the shoulder at 125 cm^{-1} in our Raman spectrum of [NMe$_4$]$^+$[AlCl$_4$]$^-$, and we accordingly adopted the force field of assignment (2) in Table 2 in the calculations we now describe.

TABLE 3

Correlation of observed bands in [NMe$_4$]$^+$[AlCl$_x$Br$_{4-x}$]$^-$ spectra with those of a UBFF field *

Mode	[AlCl$_3$Br]$^-$	[AlClBr$_3$]$^-$	Mode	[AlCl$_2$Br$_2$]$^-$
$\nu_1(a_1)$	440(443)	(478)	$\nu_1(a_1)$	465(466)
$\nu_2(a_1)$	308(308)	247(247)	$\nu_2(a_1)$	278(280)
$\nu_3(a_1)$	156?(153)	134?(132)	$\nu_3(a_1)$	(222)
$\nu_4(e)$	495(493)	400(407)	$\nu_4(a_1)$	125?(126)
$\nu_5(e)$	180? 168?	134? 144?	$\nu_5(a_1)$	(107)
	(166)	(134)		
$\nu_6(e)$	(115)	(90)	$\nu_6(b_1)$	495(489)
			$\nu_7(b_1)$	156?(153)
			$\nu_8(b_2)$	418?(412)
			$\nu_9(b_2)$	144?(142)

* Calc. values in parentheses.

With the assumption of transferability of force constants, the force fields for all five ions [AlCl$_n$Br$_{4-n}$]$^-$ require eight UBFF constants. Six of these have been obtained in the calculations for [AlCl$_4$]$^-$ and [AlBr$_4$]$^-$

and the remaining two, F_{BrCl}, and H_{BrCl}, were given the values 0·21 and 0·031 mdyne Å^{-1} by interpolation. These constants were then used to estimate the vibrational frequencies of the three ions [AlCl$_3$Br]$^-$, [AlCl$_2$Br$_2$]$^-$, and [AlClBr$_3$]$^-$ and these results are shown in Table 3.

The strongly Raman-active modes at 308, 278, and 247 cm^{-1} previously assigned by intensity considerations to [AlCl$_3$Br]$^-$, [AlCl$_2$Br$_2$]$^-$, and [AlClBr$_3$]$^-$ respectively, are seen to be predicted extremely well by the chosen UBFF, each being the $\nu_2(a_1)$ mode for its species. The two bands assigned from the i.r., 465 cm^{-1} to [AlCl$_2$Br$_2$]$^-$ and 440 cm^{-1} to [AlCl$_3$Br]$^-$ also agree very well with the calculated values of ν_1 for these ions. It therefore appears that the approximation of transferring stretching force-constants between the ions in the series is a good one, and that the remaining stretching modes in these ions should be observed in the spectra close to their calculated positions.

Thus the strong broad band at *ca.* 495 cm^{-1} presumably gains intensity not only from the band ν_4 at this frequency in [AlCl$_4$]$^-$ but also from the e mode ν_4 of [AlCl$_3$Br]$^-$ and the b_1 mode ν_6 of [AlCl$_2$Br$_2$]$^-$, predicted to occur at 493 and 489 cm^{-1} respectively. Unfortunately the ν_4 band of [AlCl$_4$]$^-$ is itself strong and broad enough in the i.r. to obscure any contributions from the other modes. Similarly the stretching frequencies predicted for ν_4 of [AlClBr$_3$]$^-$ and ν_8 of [AlCl$_2$Br$_2$]$^-$ at 407 and 412 cm^{-1} respectively cannot be reliably resolved from the strong i.r. mode ν_4 of [AlBr$_4$]$^-$ at 404 cm^{-1}. All these modes are very weak in the Raman effect, so that neither vibrational technique serves to confirm these assignments clearly. The remaining stretching mode predicted by the UBFF treatment, ν_1 of [AlClBr$_3$]$^-$ at 478 cm^{-1} is not observed.

The situation for the bending frequencies is much less satisfactory. There are no certain bending assignments for any bromochloroaluminate ions which can be used to check the validity of the transferred or interpolated bending force constants. Therefore although assignments to each ion shown in Table 3 are not unreasonable they must be regarded as highly tentative.

16 J. H. Schnachtschneider, Tech. Report No. 57—65, Shell Development Co.