Hydrogen Bonding in Imidazolium Salts and its Implications for Ambient-temperature Halogenoaluminate(III) Ionic Liquids*

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The salts [emim]X (X = Br or I, emim = 1-ethyl-3-methylimidazolium) and [emim][$AlBr_4$] have been prepared as solid-state models of the [emim]X–AlX_3 (X = Cl or Br) ionic liquid systems. All three have been characterised crystallographically. The salts [emim]X (X = Br or I) are isomorphous and are composed of ions in an extended hydrogen-bonded network. The implications of these results for both the structure and solvent properties of the ionic liquids are discussed.

Systems that form ionic liquids at, and below, room temperature, are becoming increasingly important as solvents for both organic and inorganic chemistry.[1,2] Halogenoaluminate(III)-based ionic liquids, which may be used to investigate a wide range of industrially important chemistry, have been of particular interest. In recent years the preferred systems have been those formed by mixtures of 1-ethyl-3-methylimidazolium halides ([emim]X, X = Cl or Br) with the corresponding aluminium(III) halide (AlX_3, X = Cl or Br).[3,4] The anionic distribution in these ionic liquids is dependent on their composition. In basic compositions (excess of [emim]X, X = Cl or Br), the halide ion is present in appreciable concentration. In acidic compositions $[Al_2X_7]^-$ and $[Al_3X_{10}]^-$ (X = Cl or Br) may be found.[5] The ion $[AlX_4]^-$ (X = Cl or Br) is found over the entire liquid range of these systems.

For some time, the possibility of hydrogen bonding between a potential electron-pair donor (hydrogen-bond acceptor) and the cation was a matter of some debate.[6,7] This was largely resolved, for simple halide ions, by a detailed conductimetric and NMR study of solutions of the salts [emim]X (X = Cl, Br or I) in a variety of solvents, which has been published in a companion paper.[8] However, this study did not consider alternative potential electron-pair donors. Crystallographic investigations of chlorometalate salts of the $[emim]^+$ cation, and of the related 1-ethyl-2,3-dimethylimidazolium cation, $[edmim]^+$, show that hydrogen bonding to complex ions is possible,[9,10] but is not always the case.[11]

In this paper we present the crystal structures of the salts [emim]I, which has been previously communicated,[12] [emim]Br and [emim][$AlBr_4$]. The interionic interactions are investigated, and the implications for the structure of the halogenoaluminate(III) ionic liquids, and their solvent properties, are discussed.

Experimental

Starting Materials.—1-Methylimidazole, 1-bromoethane and 1-iodoethane (all Aldrich) were used as supplied. Ethanenitrile and ethyl ethanoate (both Aldrich) were dried by distillation from P_2O_5, under dry dinitrogen, immediately prior to use. 1-Ethyl-3-methylimidazolium chloride (Merck) was used as supplied. Aluminium(III) bromide (Aldrich) was sublimed from aluminium powder and sodium bromide *in vacuo* three times, until a colourless material was obtained.

Preparations.—1-*Ethyl*-3-*methylimidazolium bromide.* 1-Methylimidazole (35 cm^3, 0.63 mol) was distilled *in vacuo* from potassium hydroxide into a round-bottomed flask (250 cm^3) fitted with a side arm. Bromoethane (90 cm^3, 0.69 mol) was added by distillation *in vacuo* from phosphorus(V) oxide. The mixture was heated under reflux under dry dinitrogen for 2 h and left to cool overnight. The resulting white solid was dissolved in hot ethanenitrile (50 cm^3) and filtered under dry dinitrogen. Dry ethyl ethanoate (100 cm^3) was added to the filtrate and the mixture cooled to −13 °C. The resulting precipitate was isolated by Schlenk filtration and recrystallised from the minimum of ethanenitrile (20 cm^3). The resulting white precipitate was isolated by Schlenk filtration, dried *in vacuo* for 36 h and transferred to a dry-box. Yield: 69.3 g (57.6%), m.p. 81 °C (lit.,[13] 81 °C) (Found: C, 37.95; H, 5.95; N, 14.40. Calc. for $C_6H_{11}BrN_2$: C, 37.70; H, 5.80; N, 14.65%).

1-*Ethyl*-3-*methylimidazolium iodide.* 1-Methylimidazole (25 cm^3, 0.45 mol) was distilled *in vacuo* from potassium hydroxide directly into a round-bottomed flask (250 cm^3) fitted with a side arm. Iodoethane (60 cm^3, 0.49 mol) was added by distillation *in vacuo* from phosphorus(V) oxide. Heat was evolved and the solution became pale yellow. The solution was heated under reflux, under dry dinitrogen, for 2 h. After this time, two immiscible layers had formed, the upper of which became a yellow solid on cooling to room temperature. The lower layer was removed by Schlenk filtration and the solid dissolved in dry ethanenitrile (40 cm^3) and then recrystallised by addition of dry ethyl ethanoate (80 cm^3). This recrystallisation procedure was repeated twice before the white precipitate was finally recrystallised from the minimum of hot, dry ethanenitrile (20 cm^3) whilst protecting the product from light. The solid was dried *in vacuo* for 36 h and transferred to a dry-box. Yield: 63.0 g (79.7%), m.p. 81 °C (lit.,[13] 79–80 °C) (Found: C, 30.05; H, 4.70; N, 11.20. Calc. for $C_6H_{11}N_2$: C, 30.25; H, 4.65; N, 11.75%).

1-*Ethyl*-3-*methylimidazolium tetrabromoaluminate*(III). Aluminium tribromide (3.06 g, 11.47 mmol) was added, with care, to [emim]Br (1.91 g, 10 mmol). The mixing process was

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

exothermic. The resulting pale yellow liquid was allowed to cool to room temperature. After several days at room temperature a few colourless crystals had formed on the surface of the liquid. One of these was collected for X-ray diffraction analysis. This procedure was repeated and the crystals used for infrared analysis.

Crystallographic Data Collection.—Crystals of [emim]Br (*ca.* 0.4 × 0.3 × 0.2 mm) and [emim]I (*ca.* 0.25 × 0.20 × 0.15 mm) were prepared by recrystallisation from solutions in dry ethanenitrile. They were isolated by Schlenk filtration and dried in a stream of dry dinitrogen. A crystal of [emim][$AlBr_4$] (*ca.* 0.2 × 0.15 × 0.10 mm) was picked directly from the melt. The crystals were mounted in Lindemann capillary tubes for structural analysis. Data were collected on an Enraf-Nonius CAD4 diffractometer, using Mo-Kα radiation (λ = 0.710 69 Å).

For [emim]I preliminary cell dimensions were found using the SEARCH and INDEX routines of the diffractometer. The structure was solved by heavy-atom methods, on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package.[14] Refinement was by full-matrix least squares with non-hydrogen atoms anisotropic and hydrogen atoms isotropic. A final difference map was featureless.

The crystals of [emim]Br were isomorphous with those of [emim]I. Starting with the coordinates from the iodide structure, refinement by full-matrix least squares, with non-hydrogen atoms anisotropic and hydrogen atoms isotropic, was used to solve the structure.

For [emim][$AlBr_4$] it was not possible to index all the reflections from the crystal. This suggests that the sample may have been twinned. However, approximately half of the reflections fitted a rational unit cell ($P2_1/c$). The reflections were broad, and the cell parameters are, therefore, of rather low accuracy. Also, the higher-angle reflections were uniformly weak. Non-hydrogen atoms were located by direct methods (Al and Br), and a Fourier-difference map (N and C). Refinement was by full-matrix least squares with Br anisotropic and Al, N and C isotropic. Hydrogen atoms were omitted.

For both [emim]Br and [emim][$AlBr_4$], programs from the Enraf-Nonius SDP-Plus package were run on a Microvax II computer. A summary of the crystal data is given in Table 6, final atomic coordinates in Tables 7–9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Infrared Spectra.—The infrared spectra of the salts [emim]X (X = Cl, Br or I) and [emim][$AlBr_4$] were recorded in the region 4000–2000 cm^{-1} as hexachlorobutadiene mulls on sodium chloride plates. This allows the C–H stretching vibrations to be observed (Table 1, Fig. 1).

In the spectrum of [emim][$AlBr_4$] the peak at 3124 cm^{-1} can be attributed to the ring C–H stretch, whilst those below 3000 cm^{-1} can be attributed to aliphatic C–H stretches.[6] In the spectra of the salts [emim]X (X = Cl, Br or I) a new peak between 3050 and 3080 cm^{-1} has appeared and the peak at *ca.* 3130 cm^{-1} has considerably diminished. For the iodide salt, this new band has resolved into two peaks, indicating that there are two types of hydrogen bonds of different strength. This is in good agreement with the crystallographic data (see below). In addition a series of weak absorptions between 2500 and 2850 cm^{-1} can be seen (see Fig. 1 for an example spectrum of [emim]I). Both of these effects may be attributed to the formation of hydrogen bonds between the aromatic protons and the halide ions. Upon the formation of a C–H $\cdots$ X$^-$ hydrogen bond the C–H bond is weakened and the frequency of its stretching vibration is decreased; this is usually accompanied by an increase in intensity and a broadening of the band.[15] It is this vibration that is responsible for the new peak seen in the spectra of the simple halide salts. Anharmonicity is manifested as the series of weak peaks between 2500 and 2850 cm^{-1}.[16] The C–H $\cdots$ X$^-$ system has three fundamental vibrational modes, the C–H stretch ν_1, the C–H $\cdots$ X$^-$ bend ν_2, which is split into in-plane and out-of-plane motions for non-linear systems, and the CH $\cdots$ X$^-$ stretch ν_3. It is combinations of these modes, principally between ν_1 and ν_3, that lead to the bands seen. This is often referred to as the Sheppard effect.[16]

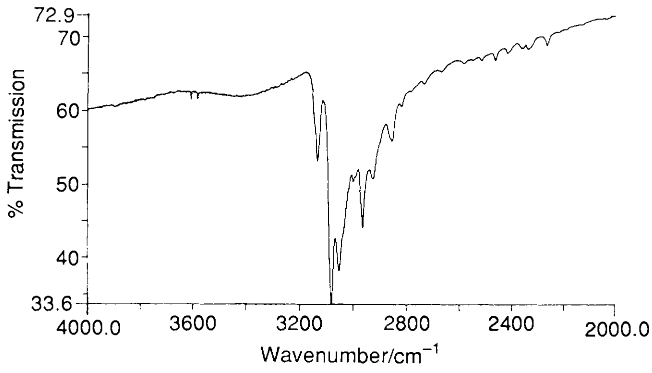

Fig. 1 Infrared spectrum of [emim]I (4000–2000 cm^{-1})

Table 1 Infrared spectral data (4000–2000 cm^{-1}, hexachlorobutadiene mull) of [emim]X (X = Cl, Br, I or $AlBr_4$)

$\tilde{\nu}$/cm^{-1}

Cl$^-$	Br$^-$	I$^-$	[$AlBr_4$]$^-$	Assignment
3135w	3137m	3133m	3124vs	Aromatic C–H str.
3154s	3064vs	3080vs, 3052s		Aromatic C–H str.
2962vs	2959vs	2963vs	2961s	Aliphatic C–H str.
2927s	2925s	2926s	2923m	Aliphatic C–H str.
2856m	2858m	2854m	2852m	Aliphatic C–H str.
2850– 2500w	2850– 2500w	2850– 2500w		Overtone and combination bands due to hydrogen bonding

It is difficult to make a simple correlation between the changes seen in the C–H stretching frequency in the infrared spectra and the precise energy of the hydrogen bond, but the behaviour seen is typical of systems with a hydrogen bond of energy up to *ca.* 25 kJ mol^{-1}.[15] It is, however, clear that the extent of shift in the positions of the C–H stretching band shows that the strength of the interaction decreases in the order Cl$^-$ > Br$^-$ > I$^-$. This is in good agreement with NMR data.[8]

Crystallographic Data.—Throughout the crystallographic discussion the individual atoms are given two labels: those derived from the systematic ring numbering of the compounds, and crystallographic labels in the form X(*n*) {*e.g.* H(1) is equivalent to H^5 in the [emim]Br structure}.

The [emim]$^+$ *cation.* The [emim]$^+$ cation (Fig. 2) is common to all three of the salts presented here. This presents an opportunity to compare its structure in a variety of different crystals. The dimensions of the carbon–nitrogen skeleton (Tables 2–4) do not vary significantly between the three structures; although the precision of the bond lengths in [emim][$AlBr_4$] is poor, their values are of the same order as those of [emim]X (X = Br or I). Comparison with other crystal structures of 1-ethyl-3-methylimidazolium salts reveals that the internal dimensions of the [emim]$^+$ cation are largely insensitive to the local environment.[10,11] This is in direct contradiction to the findings of a single-crystal study of [emim]Cl,[17] and reflects the poor-quality data for this latter structure. The imidazolium ring is a planar pentagon, with two pairs of C–N bonds, the C^2–N bonds being shorter than

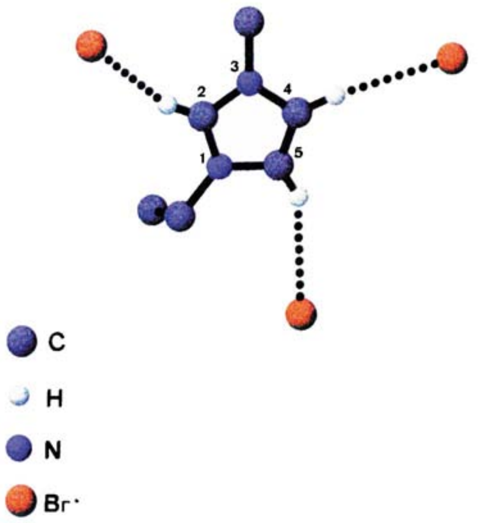

Fig. 2 Local structure around a single cation in [emim]X (X = Br or I)

Table 2 Intramolecular distances (nm) and angles (°) for [emim]I, with estimated standard deviations (e.s.d.s) in parentheses

N(1)–C(1)	0.1374(5)	N(1)–C(2)	0.1324(5)
N(1)–C(5)	0.1476(7)	N(2)–C(2)	0.1315(6)
N(2)–C(3)	0.1369(4)	N(2)–C(4)	0.1461(5)
C(1)–C(3)	0.1322(7)		
C(1)–N(1)–C(2)	107.7(4)	C(1)–N(1)–C(5)	126.4(3)
C(2)–N(1)–C(5)	125.9(3)	C(2)–N(2)–C(3)	108.1(3)
C(2)–N(2)–C(4)	123.8(3)	C(3)–N(2)–C(4)	128.0(4)
N(1)–C(1)–C(3)	107.4(3)	N(1)–C(2)–N(2)	109.1(3)
N(2)–C(3)–C(1)	107.7(4)	N(1)–C(5)–C(6)	111.5(5)

Table 3 Intramolecular distances (nm) and angles (°) for [emim]Br, with e.s.d.s in parentheses

N(1)–C(1)	0.1377(5)	N(1)–C(2)	0.1327(5)
N(1)–C(5)	0.1488(7)	N(2)–C(2)	0.1323(6)
N(2)–C(3)	0.1368(4)	N(2)–C(4)	0.1449(5)
C(1)–C(3)	0.1351(6)		
C(1)–N(1)–C(2)	108.7(3)	C(1)–N(1)–C(5)	125.3(3)
C(2)–N(1)–C(5)	125.9(3)	C(2)–N(2)–C(3)	108.8(3)
C(2)–N(2)–C(4)	125.0(3)	C(3)–N(2)–C(4)	126.1(4)
N(1)–C(1)–C(3)	106.5(3)	N(1)–C(2)–N(2)	108.6(3)
N(2)–C(3)–C(1)	107.4(4)	N(1)–C(5)–C(6)	111.6(4)

the C^4–N and C^5–N. The ethyl group of the cation lies such that the β-carbon is out of the plane of the imidazolium ring. Again this is common.[10,11,17] Even in structures where the hydrogen atoms have been located and included in refinements there is considerable variation in C–H bond lengths. It would not, therefore, be safe to comment on the effects of the local environment on these bonds on the basis of currently available data.

The $[AlBr_4]^-$ *anion.* The $[AlBr_4]^-$ anion is a simple tetrahedron, with a mean Al–Br bond length of 0.2291 nm and Br–Al–Br angle of 109.5°. This is entirely consistent with literature values.[18–20]

Interionic interactions. The crystals of [emim]I and [emim]Br are isomorphous, and are discussed together. The structures consist of layers of anions and cations which are interconnected by an extended network of hydrogen bonds (Fig. 3). Each cation is hydrogen bonded to three anions (Figs. 2 and 4, Table 5) and each anion is hydrogen bonded to three cations. The $H^4 \cdots X^-$ and $H^5 \cdots X^-$ contacts are considerably shorter than the $H^2 \cdots X^-$, indicating weaker hydrogen bonds. Indeed, the hydrogen bonding at the H^4 and H^5 ring protons was not recognised in the previous communication of

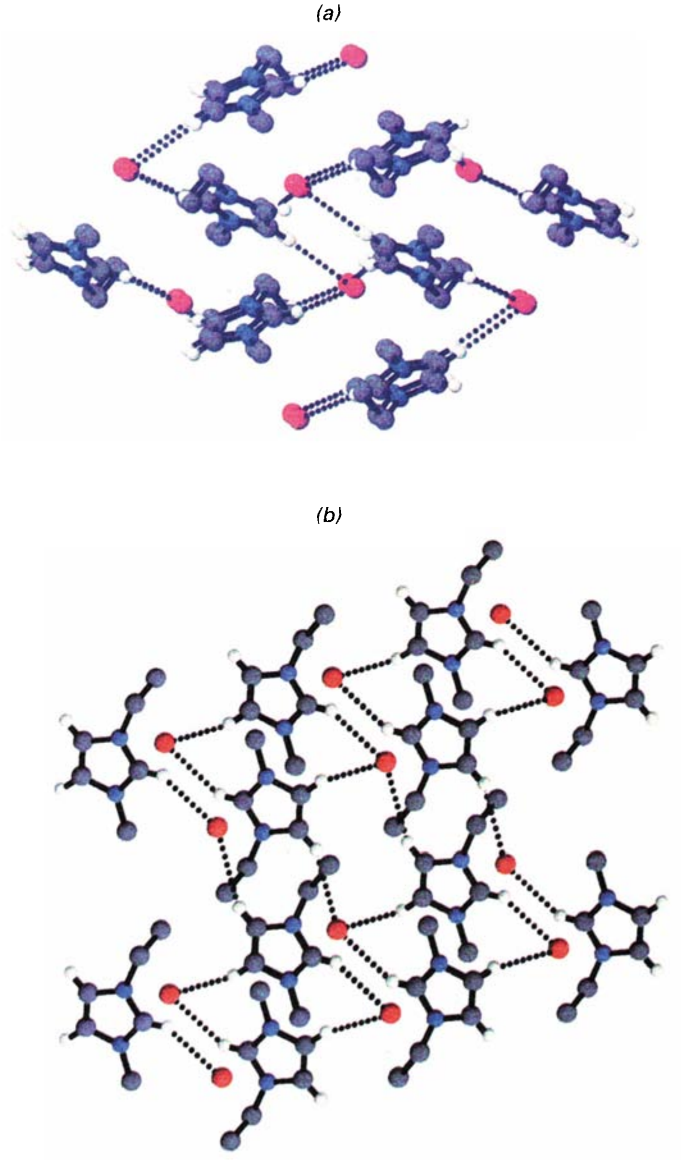

Fig. 3 Packing of ions in [emim]X (X = Br or I), viewed down the *a* (*a*) and *b* axes (*b*)

Table 4 Intramolecular distances (nm) and angles (°) for [emim]-$[AlBr_4]$, with e.s.d.s in parentheses

Br(1)–Al	0.2287(14)	Br(2)–Al	0.2288(12)
Br(3)–Al	0.2296(15)	Br(4)–Al	0.2292(12)
N(1)–C(1)	0.131(5)	N(1)–C(3)	0.142(5)
N(1)–C(5)	0.148(5)	N(2)–C(1)	0.128(5)
N(2)–C(2)	0.139(6)	N(2)–C(4)	0.145(5)
C(2)–C(3)	0.130(6)	C(5)–C(6)	0.157(6)
Br(1)–Al–Br(2)	110.0(6)	Br(1)–Al–Br(3)	110.9(5)
Br(1)–Al–Br(4)	109.8(6)	Br(2)–Al–Br(3)	109.1(6)
Br(2)–Al–Br(4)	108.8(5)	Br(3)–Al–Br(4)	108.2(6)
C(1)–N(1)–C(3)	111(3)	C(1)–N(1)–C(5)	123(3)
C(3)–N(1)–C(5)	126(3)	C(1)–N(2)–C(2)	107(3)
C(2)–N(2)–C(4)	128(3)	C(1)–N(2)–C(4)	125(3)
N(1)–C(1)–N(2)	108(3)	N(2)–C(2)–C(3)	112(4)
N(1)–C(3)–C(2)	101(4)	N(1)–C(5)–C(6)	108(3)

Fig. 4 Local structure around a single anion in [emim]X (X = Br or I)

Table 5 Contacts H $\cdots$ X and C $\cdots$ X (nm) in, or near to, the plane of the imidazolium ring

	Br^-	I^-	$[AlBr_4]^-$
$H^5 \cdots X$	0.297	0.317	—
$H^2 \cdots X$	0.278	0.293	—
$H^4 \cdots X$	0.289	0.313	—
$C^5 \cdots X$	0.3817	0.4028	0.3762
$C^2 \cdots X$	0.3575	0.3671	0.4010
$C^4 \cdots X$	0.3820	0.4028	0.3997

the structure of [emim]I.[12] If only the bonds at H^4 and H^5 of the imidazolium ring are considered, a ring structure reminiscent of that in [edmim]Cl is observed.[9] It is probable that this arrangement is particularly favourable. The local structure around the cation is superficially similar to that observed for [emim]Cl, but the overall morphology of the crystals is somewhat different.[17] In [emim]X (X = Br or I) there is only one unique cation and one unique anion, whereas in [emim]Cl there are four unique cations and four unique anions. In [emim]X (X = Br or I) each anion is hydrogen bonded to three cations, one by the H^2, one by the H^4 and one by the H^5 proton of the imidazolium ring. However, in [emim]Cl the arrangement is considerably more complicated. Each of the crystallographically distinct chloride ions is hydrogen bonded to three cations, but to different ring protons. One chloride ion is bonded to the H^4 proton of one cation and to the H^2 protons of two other cations, the next is bonded to the H^4 protons of two cations and to the H^2 proton of the third cation, the next is bonded to the H^4 proton of one cation and to the H^5 protons of two cations and the final chloride is bonded to the H^2 proton of one cation and to the H^5 proton of two cations. This leads to an overall structure that is considerably more disordered than those of the bromide and iodide salts.

It is tempting to infer that the greater disorder found in the structure of [emim]Cl is responsible for the formation of the [emim]Cl–$AlCl_3$ ionic liquids. However, the melting points of the three salts are remarkably similar ([emim]Cl 84; [emim]Br 81; [emim]I 81 °C), and it should not be forgotten that [emim]Br–$AlBr_3$ ionic liquids have been described.[21] The possibility that the chloride structure represented a high-temperature polymorph, and that at lower temperatures a structure that was isostructural with the bromide and iodide might be formed, was considered. However, DSC measurements (20–100 °C) failed to show solid-state phase transitions for any of the three salts. Hence, there is no evidence for a transition to a chloride-like structure for the bromide and iodide salts before they melt. It is therefore unlikely that the chloride salt has a low-temperature polymorph which is isostructural with the bromide and iodide structures. Probably, size differences of the halide ions are responsible for the different structures adopted by the salts.

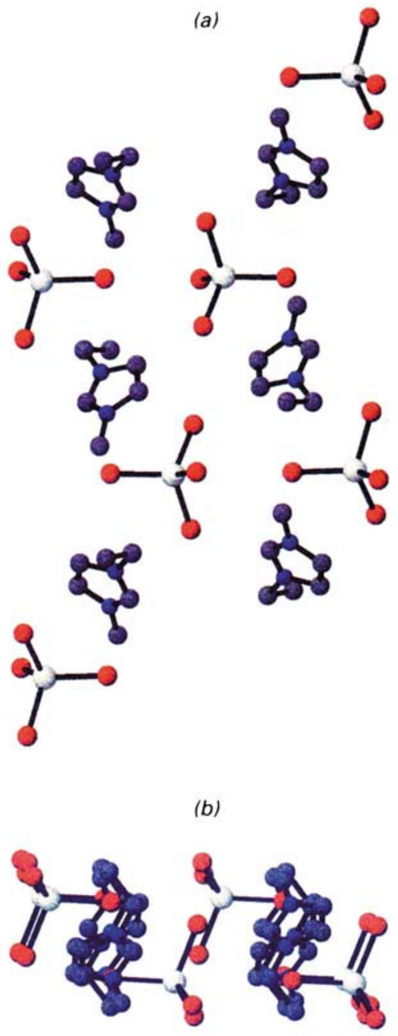

Fig. 5 Packing of ions in [emim][$AlBr_4$], viewed down the *a* (*a*) and *b* axes (*b*)

The data for [emim][$AlBr_4$] are of poor quality and the protons have not been located. It is therefore difficult to make any definitive statements about hydrogen-bonding interactions. However, comparison of C $\cdots$ Br contacts in, or near to, the plane of the imidazolium ring in [emim][$AlBr_4$] (Table 5) with those in [emim]Br suggests that hydrogen bonding to the $[AlBr_4]^-$ is unlikely. In addition, the structure of the salt $[Hpy]_3Br[AlBr_4]_2$ (py = pyridine) has shown that the $[AlBr_4]^-$ ion is a poor hydrogen-bond acceptor.[20] It is, therefore, extremely unlikely that there is any hydrogen-bond formation in [emim][$AlBr_4$]. This is in accord with predictions based on the structures of transition-metal salts of this cation.[10]

In crystals of [emim][$AlBr_4$] layers of anions and cations, lying in the *ab* plane, alternate through the structure. As can be seen (Fig. 5), there is some interpenetration of the planes. The shortest C $\cdots$ Br contacts (0.3363–0.4422 nm) are to anions above and below the plane of the imidazolium ring. Since this direction allows direct contact between the carbon and bromine atoms, without intervening protons, this probably arises from simple packing constraints. Further to this, the orientation of the cations towards the anions vary, with some presenting the face and others the edge of the imidazolium ring. Hence, it is unlikely that any specific cation–anion interactions occur.

Conclusion

All three of the simple halide salts [emim]X (X = Cl, Br or I) form cation–anion hydrogen bonds. As AlX_3 (X = Cl or Br) is

Table 6 Summary of the crystallographic experimental conditions, data collection and refinements[a]

	[emim]Br	[emim]I	$[emim][AlBr_4]$
Chemical formula	$C_6H_{11}BrN_2$	$C_6H_{11}IN_2$	$C_6H_{11}AlBr_4N_2$
M	191.1	238.07	457.8
a/nm	0.8749(1)	0.8789(3)	0.7180(10)
b/nm	0.7999(1)	0.8130(3)	1.4373(30)
c/nm	1.2662(5)	1.3364(3)	1.3259(30)
β/°	109.91(2)	107.33(2)	91.29(15)
U/nm^3	0.8332	0.9117	1.3680
F(000)	384	456	856
$D_c/g\ cm^{-3}$	1.52	1.734	2.22
μ/cm^{-1}	48.1	34.05	116.9
θ limits/°	2–25	2–23	2–25
Total reflections collected	1578	*b*	2393
Maximum, minimum absorption correction	1.19, 0.72	—	1.71, 0.76
No. of reflections $[I > \sigma(I)]$	965	1089	746
Final *R*	0.030	0.023	0.078
Final *R*′	0.038	0.028	0.095

[a] Details in common: monoclinic, space group $P2_1/c$; $Z = 4$; *h*, *k*, ± *l* collected; scan mode θ–2θ; $w^{-1} = \sigma^2(F)$. [b] Not recorded.

Table 7 Fractional atomic coordinates (× 10^4, except H × 10^3) for [emim]I, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
I	7 975(4)	2 130(6)	9 263(5)
N(1) N^1	12 958(4)	3 191(4)	12 079(3)
N(2) N^3	10 813(4)	4 317(4)	12 211(2)
C(1) C^5	13 277(5)	3 794(6)	13 081(3)
C(2) C^2	11 456(4)	3 547(6)	11 572(3)
C(3) C^4	11 953(5)	4 478(6)	13 160(3)
C(4) NCH_3	9 186(5)	4 960(7)	11 897(3)
C(5) $\mathit{C}\mathrm{H_2CH_3}$	14 090(6)	2 332(7)	11 637(4)
C(6) $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$	14 765(7)	3 455(10)	11 013(5)
H(1) H^5	1 428(4)	368(5)	1 355(3)
H(2) H^2	1 096(5)	312(5)	1 081(3)
H(3) H^4	1 175(4)	502(5)	1 373(3)
H(4a) CH_3	898(4)	508(6)	1 239(3)
H(4b) CH_3	854(6)	441(7)	1 123(4)
H(4c) CH_3	924(6)	618(7)	1 172(4)
H(5a) $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$	1 345(7)	99(8)	1 133(4)
H(5b) $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$	1 494(8)	200(8)	1 236(5)
H(6a) $\mathrm{CH_2C}\mathit{H}_3$	1 555(7)	291(7)	1 063(5)
H(6b) $\mathrm{CH_2C}\mathit{H}_3$	1 391(5)	375(5)	1 021(3)
H(6c) $\mathrm{CH_2C}\mathit{H}_3$	1 521(5)	438(7)	1 161(3)

Table 8 Fractional atomic coordinates (× 10^4, except H × 10^3) for [emim]Br, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Br	7 929.4(5)	2 154.8(6)	9 240.5(3)
N(1) N^1	12 949(3)	3 147(4)	12 080(3)
N(2) N^3	10 815(3)	4 323(4)	12 221(2)
C(1) C^5	13 283(5)	3 800(5)	13 147(3)
C(2) C^2	11 394(4)	3 489(5)	11 537(3)
C(3) C^4	12 038(4)	4 540(6)	13 227(3)
C(4) NCH_3	9 175(5)	4 970(7)	11 920(4)
C(5) $\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$	14 066(5)	2 270(6)	11 602(4)
C(6) $\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$	14 753(5)	3 425(7)	10 976(4)
H(1) H^5	1 444(4)	371(5)	1 365(3)
H(2) H^2	1 081(5)	324(5)	1 083(3)
H(3) H^4	1 183(4)	509(5)	1 384(3)
H(4a) NCH_3	902(5)	470(7)	1 260(4)
H(4b) NCH_3	866(6)	469(7)	1 131(4)
H(4c) NCH_3	920(6)	634(8)	1 175(5)
H(5a) $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$	1 348(5)	138(6)	1 112(3)
H(5b) $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$	1 495(7)	174(9)	1 242(6)
H(6a) $\mathrm{NCH_2C}\mathit{H}_3$	1 546(5)	281(6)	1 062(4)
H(6b) $\mathrm{NCH_2C}\mathit{H}_3$	1 404(5)	391(7)	1 049(4)
H(6c) $\mathrm{NCH_2C}\mathit{H}_3$	1 535(5)	438(7)	1 140(4)

Table 9 Fractional atomic coordinates (× 10^4) for $[emim][AlBr_4]$, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Br(1)	8965(6)	3648(3)	4929(3)
Br(2)	4171(6)	2615(3)	4915(3)
Br(3)	8305(6)	1043(3)	4821(4)
Br(4)	7004(5)	2501(4)	2601(3)
Al	7128(16)	2462(11)	4329(8)
N(1) N^1	5248(41)	5099(23)	2345(23)
N(2) N^3	3062(45)	4139(26)	2447(26)
C(1) C^2	4461(49)	4373(26)	1922(28)
C(2) C^4	3127(58)	4679(32)	3318(35)
C(3) C^5	4455(53)	5297(30)	3292(32)
C(4) NCH_3	1838(52)	3361(30)	2218(29)
C(5) $\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$	6808(57)	5613(31)	1893(33)
C(6) $\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$	8543(59)	5552(33)	2636(34)

added to the appropriate salt the hydrogen-bond network is disrupted and ionic liquids are formed. In basic ionic liquids the extent of hydrogen bonding is still significant. As the liquids are made more acidic the hydrogen-bond acceptor X^- is replaced by $[AlX_4]^-$ and then $[Al_2X_7]^-$ (X = Cl or Br), until no hydrogen bonds are present.

The ability of a solvent to form hydrogen bonds with potential solutes is an important feature of its behaviour. Basic $[emim]X–AlX_3$ (X = Cl or Br) ionic liquids can act as both hydrogen-bond acceptor (X^-) and donor ($[emim]^+$), and would be expected to stabilise solutes which have both accepting and donating sites. However, it must be remembered that there will be competition between the solute and solvent ions. Acidic compositions can act as a hydrogen-bond donor ($[emim]^+$), but not as an acceptor. Hence they would be expected to stabilise solutes with hydrogen-bond acceptor sites.

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