Structure of 1-Ethyl-3-methylimidazolium Hexafluorophosphate: Model for Room Temperature Molten Salts

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The crystal structure of 1-ethyl-3-methylimidazolium (EMI^+) hexafluorophosphate consists of interionic interactions dominated by cation–anion coulombic forces with minimal hydrogen bonding and serves as a model for EMI^+ room temperature molten salts containing weakly complexing anions.

Room temperature molten salts formed by combining 1-ethyl-3-methylimidazolium chloride (EMIC) and $AlCl_3$ are versatile solvents for chemical and electrochemical processes.[1] When EMIC and $AlCl_3$ are combined in a 1:1 molar ratio, the resulting molten salt has the formula $(EMI^+)(AlCl_4^-)$, **1**, and possesses a wide electrochemical window.[2] In addition, alkali metal chlorides can be substituted for a portion of the EMIC to produce the room temperature melts $(EMI^+)_{1-x}(M^+)_x(AlCl_4^-)$ (M = Li, Na, K, Rb, Cs).[3] Melts containing Li^+ or Na^+ have recently come under close scrutiny as electrolytes for lithium or sodium secondary batteries.[4] More recently, a similar room temperature molten salt $(EMI^+)(BF_4^-)$, **2**, has been reported.[5] This melt has the desirable property of being fully air stable, a property lacking in the chloroaluminate systems.

The ability of EMI^+ to produce room temperature molten salts with $AlCl_4^-$ and BF_4^- is an intriguing and useful property and is rooted in the cation–anion interactions. Although several salt structures containing EMI^+ have been reported, all these contain anions which form substantial hydrogen bonds with the cation.[5,6] The weakly complexing anions $AlCl_4^-$ and BF_4^- are not expected to participate in strong hydrogen bonding, and this has been demonstrated for several $AlCl_4^-$ organic salts.[7] To gain insight into the interionic interactions of **1** and **2**, we have synthesized and structurally characterized the low-melting salt $(EMI^+)(PF_6^-)$, **3**, mp 58–60 °C. Like the BF_4^- room temperature melt, it is also air stable and may be useful as an electrolyte for operation at moderately elevated temperatures. Also, because PF_6^- is a weakly complexing anion, it is expected to interact with EMI^+ in a similar manner as $AlCl_4^-$ and BF_4^-. For theoretical modelling and for developing logical approaches to modifying the physical properties (melting points, conductivities, *etc.*) of low melting salts, it is essential to begin with a model possessing valid ionic, covalent and van der Waal interactions within the solid and liquid states. The crystal structure of **3** is, therefore, important because it provides direct insight into the interionic interactions in the solid state. Through proper spectroscopic comparisons, the structure of **3** can be related to the liquid state local structure found for the room temperature molten salts, **1** and **2**.

Salt **3** was synthesized by combining 29.3 g EMIC (0.2 mol) and 29.2 g 60% aqueous HPF_6 (0.2 mol) in 300 ml of water. The resulting solution and white precipitate were cooled for 2 h in an ice bath, then filtered to give 31.8 g of **3** (62% yield). Crystals suitable for X-ray structural analysis were obtained by recrystallizing the salt from methanol.†

The molecular structure of **3** is shown in Fig. 1, and the ion packing is illustrated in Figs. 2 and 3. The organic cations are positioned in pairs with a centroid to centroid separation of 5.39 Å, and a plane to plane separation of 4.53 Å. As shown in Fig. 3, the cations exhibit a large parallel offset and are not in a stacked arrangement. The PF_6^- anions in **3** surround the organic cations, and the fluorine atoms partially penetrate the region between the two cations at sites away from the ethyl groups. The ethyl groups also extend into the region between the two cations. The long distances between cations, and the lack of a stacked structure, precludes any possibility of π–π aromatic interactions as has been proposed for 1-methylimi-

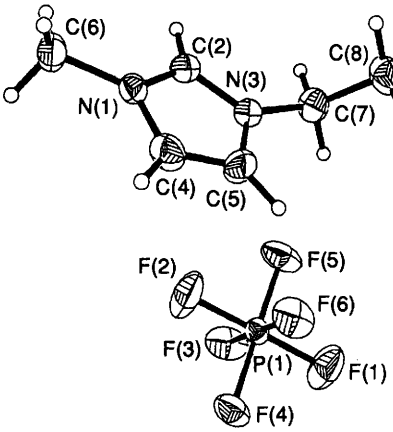

Fig. 1 Molecular structure of **3**

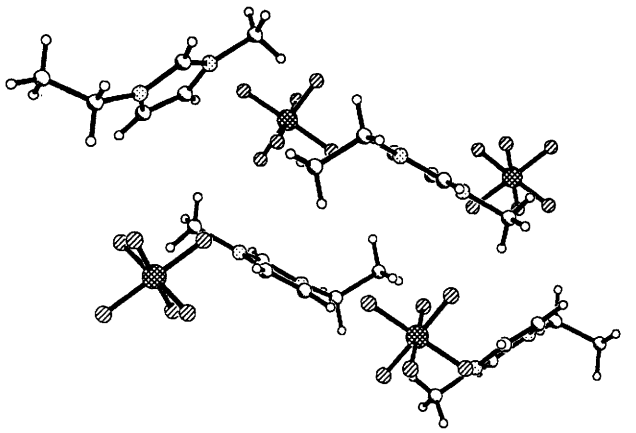

Fig. 2 View of **3** showing the PF_6^- anions surrounding the organic cations

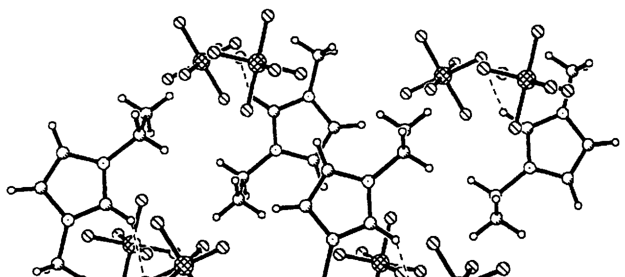

Fig. 3 View of **3** showing the parallel offset of the two cations and the weak hydrogen bonding between the C(2) hydrogen and a fluorine atom

Table 1 Hydrogen bond lengths and angles for **3**

Bond distances[a]	(Å)	Bond angles	(degrees)
H2A···F5(a)	2.559	C2–H2A···F5(a)	128.8
H2A···F2(a)	2.678	C2–H2A···F2(a)	157.1
H2A···F3(b)	2.697	C2–H2A···F3(b)	106.9
H5A···F1(c)	2.690	C5–H5A···F1(c)	132.8
H6B···F6(d)	2.644	C6–H6B···F6(d)	119.2
H6A···F5(a)	2.652	C6–H6A···F5(a)	135.7

[a] Letter in parentheses indicates PF_6^- units related by symmetry elements.

dazolium salts containing cation–anion hydrogen bonding.[8] The structure of **3** shows the importance of the ethyl groups as it maintains a hydrophobic region separate from the more ionic region around the PF_6^- unit. Combined with the weak interactions between PF_6^- and EMI^+, the structure would appear to be accommodating to both hydrophobic molecules (aromatics are known to be miscible with **1**[1]) and other ionic species ($LiBF_4$ is soluble in **2** to at least 100 mmol dm^{-3}).

Generally, the criteria for the presence of Y–H···X hydrogen bonding is that the H···X distance must be less than the sum of the H and X van der Waals radii, and the Y–H···X angle must be greater than 90°.[9] Taking the van der Waals radii to be 1.20 and 1.50 Å for hydrogen and fluorine, respectively, the C–H···F distances less than 2.70 Å are indicative of hydrogen bonding.[10] Table 1 lists all distances and angles for H···F distances less than 2.70 Å. The shortest H···F distance, 2.557 Å, is to the C2 ring hydrogen and is indicated by dashed lines in Fig. 3. This is not unexpected, since this hydrogen forms strong hydrogen bonds in several other EMI^+ salts.[5,6] Even though the H2A···F5(a) distance is well within the sum of the van der Waals radii, it is still a relatively weak interaction as indicated by the lack of a hydrogen-bonding band in the IR spectrum of **3** (see below). The other distances given in Table 1 are near the sum of the van der Waals radii and are probably not hydrogen bonds. We have also synthesized **2** using a modified preparation to produce large quantities of this room temperature melt for physical characterization.‡ The IR spectra of **2** (neat liquid) and **3** (KBr pellet) show no hydrogen-bonding bands in the region 3000–3100 cm^{-1} where C–H···Cl^- interactions in chloride-rich $AlCl_3$–EMIC melts have been observed previously.[11] The $AlCl_4^-$ salt **1** also shows no hydrogen-bonding bands in this region.[11] Therefore, the IR results are consistent with a lack of hydrogen bonding in all of these salts containing weakly complexing anions.

The lack of hydrogen bonding and aromatic π–π stacking in **3**, leads to the conclusion that cation–anion coulombic attraction is driving the overall crystal structure, with local steric effects influencing the final orientation. It is also possible that hydrophobic effects play a role in the orientation of the ethyl groups. Because **1** and **2** also contain weakly complexing anions and have similar IR spectra as **3**, the local liquid structures of these room temperature molten salts will likely resemble the solid state structure of **3**.

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Footnotes

† *Crystal data* for **3**: $M = 256.1$, monoclinic, $P2_1/c$, $a = 8.757(2)$, $b = 9.343(2)$, $c = 13.701(3)$ Å, $\beta = 103.05(3)°$, $U = 1092.0(4)$ Å^3, $Z = 4$, $D_c = 1.558$ g cm^{-3}. $D_m = 1.54$ g cm^{-3}, $\mu = 2.98$ cm^{-1}, crystal dimensions 0.8 × 0.8 × 0.2 mm. 1194 Reflections with $I > 4\sigma(I)$ converged at $R = 0.065$. All data were collected on a Siemens P3/PC diffractometer at 23 °C. A Siemens SHELXTL Plus (PC Version) solutions package was used to solve and refine the structure. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ 23.2 g Solid Ag_2O (0.1 mol) was stirred with 36.9 g 48% aqueous HBF_4 (0.2 mol) in 300 ml of water until the Ag_2O had reacted completely giving a clear solution. 29.3 g EMIC (0.2 mol) dissolved in water was then added to the solution. After 2 h of stirring, the AgCl precipitate was filtered off, and the filtrate was concentrate with a roto-evaporator. The resulting clear, colourless solution was dried overnight in a vacuum oven at 60 °C to give 33.6 g of **2** (85% yield).

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