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Structural Studies of Crystalline 1-Alkyl-3-Methylimidazolium Chloride Salts

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The structures of three long alkyl chain imidazolium chloride salts have been determined by X-ray diffraction; one of the salts was isolated as two polymorphs. These compounds consist of regions containing interdigitated linear alkyl chains alternating with regions containing imidazolium headgroups, chloride ions, and solvent. The arrangement of the cation headgroup and the alkyl chain is strongly dependent on the thermal history of the salt and whether the C(2) position on the imidazolium ring is methylated or protiated. Structures are found where the headgroups within the same crystal are in different environments leading to a double bilayer structure which collapses on heating.

Introduction

Various ionic liquids, i.e., liquids comprising exclusively ions, particularly those based on imidazolium cations such as 1-alkyl-3-methylimidazolium, $[C_n\text{-mim}]^+$, and 1-alkyl-2,3-dimethylimidazolium, $[C_n\text{-dmim}]^+$, have been extensively investigated over the last several years. Their properties have led to the use of ionic liquids as environmentally benign solvents for applications in "green chemistry".[1−3] Furthermore, there is considerable interest in the structural features of ionic-liquid-crystals,[4] for example, as oriented solvents which can impart selectivity in reactions by ordering reactants,[5] as templates for the synthesis of mesoporous and zeolitic materials,[6,7] and in the formation of ordered thin films.[8,9]

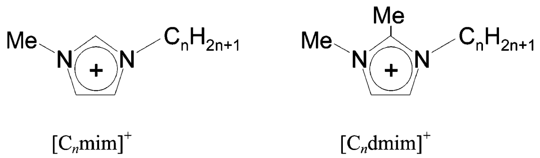

Figure 1. General structure of the cations studied: $[C_n\text{-mim}]X$ ($n = 14$ or 18) and $[C_n\text{-dmim}]X$ ($n = 18$).

Although both the field and phenomenon of room-temperature ionic liquids are now well established, much fundamental work remains to be done in fulfilling the potential of these fluids as "designer solvents". Various ionic liquids have undergone extensive investigation in a myriad of settings over the last several years,[10] particularly those based on imidazolium cations such as 1-alkyl-3-methylimidazolium,[11] $[C_n\text{-mim}]^+$, and 1-alkyl-2,3-dimethylimidazolium,[12] $[C_n\text{-dmim}]^+$, Figure 1. These liquids are typically made from imidazolium halides and it is, therefore, somewhat surprising that knowledge of the structural behavior of these intermediates (especially for alkyl chain lengths $n \geq 6$) is limited. Previously reported crystal structures include only cations with shorter chain lengths, e.g. $[C_2\text{-mim}]X$ ($X = Cl$,[13] Br,[14] I[15]), $[C_n\text{-dmim}]Cl$[16,17] ($n = 2, 3$), $[C_3$-

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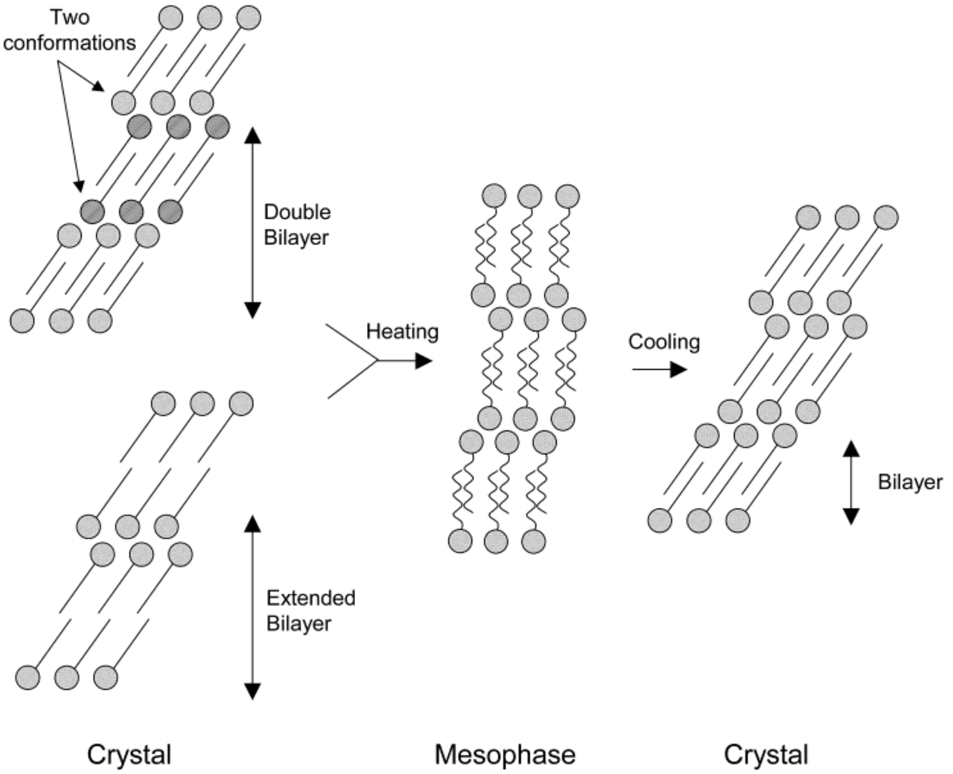

Figure 2. Schematic of the melting of the double and extended bilayer structures in the crystalline phase of, for example, [C_{14}-mim]Cl to the mesophase and subsequent recrystallization from the melt. Reproduced with permission from ref 24. Copyright 2002 American Chemical Society.

dmim]Br,[14] and [C_4-mim]Cl.[14] Published structures containing imidazolium cations with chain lengths $n \geq 6$ are limited to two hexafluorophosphate salts, [C_{12}-mim][PF_6][18] and [C_{14}-mim][PF_6],[19] and one nitrate salt [C_{14}-Him][NO_3] (C_{14}-Him = tetradecylimidazolium).[20] This overall paucity of information is particularly significant in view of observed trends in melting point with respect to alkyl chain length for [C_n-mim]Cl[11b,21,22] and [C_n-dmim]Cl[12,23] ($n = 2-18$); minima occur around $n = 7-8$ in both cases, suggesting that the solid-state structures of short- and long-chain salts differ significantly.

We recently showed that in the [C_n-mim]$^+$ ($n = 12-18$) chlorides and bromides, a peak in the SAXS data is found at low angles (approximately 1−2° 2θ).[24] The low-angle peak is consistent with a d spacing of 50−60 Å which was attributed to a double bilayer structure. However, on cooling from the isotropic liquid, a peak is observed corresponding to a d spacing of 25−31 Å. In our original paper[24] two alternative structural models were proposed to explain the large change in periodicity, either a double bilayer structure with interdigitated alkyl chains or an extended bilayer in which the alkyl chains are not interdigitated but packed end-to-end, shown schematically in Figure 2. The double bilayer model relies on differing conformations of the head-groups in alternating layers. Crystal packing allows the two conformers to be present in the unannealed form, whereas following annealing only the lowest energy species crystallizes resulting in a single conformation. In these materials, the annealed salts also showed significantly lower transition temperatures (and melting enthalpy) compared with their respective unannealed materials, indicating that there is significant structural stabilization derived from hydrogen-bonding with water in these systems.

To examine the postulated double bilayer model and the possible structural stabilization derived from hydrogen bonding between the Cl^- anions and water molecule we have obtained single-crystal data on the [C_{18}-mim]Cl·H_2O (**1**), [C_{18}-dmim]Cl·H_2O·$CHCl_3$ (**2**), and two polymorphs of [C_{14}-mim]Cl·H_2O (**3-I**) and (**3-II**).

Experimental Section

The preparation of 1-alkyl-3-methylimidazolium chlorides via the reaction of methylimidazole with a slight excess of 1-chloroalkane has been described elsewhere.[24] The "C(2) protected" 1,2-dimethyl-3-alkylimidazolium chlorides, wherein the most acidic proton of imidazolium is replaced by a methyl group, was synthesized similarly via the reaction of 1-chloroalkanes with 1,2-dimethylimidazole. Crystals of [C_{18}-mim]Cl·H_2O suitable for study by single-crystal X-ray diffraction were produced by dissolving the bulk material in 1,2-dichloroethane followed by slow evaporation of the solvent at room temperature. Crystals of [C_{18}-dmim]Cl·H_2O·$CHCl_3$ suitable for study by single-crystal X-ray diffraction were produced by dissolving

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Table 1. Crystal Data for Compounds 1, 2, 3-I, and 3-II

	$C_{22}H_{45}N_2ClO$ (**1**)	$C_{24}H_{48}Cl_4N_2O$ (**2**)	$C_{18}H_{37}N_2ClO$ (**3-I**)	$C_{18}H_{37}N_2ClO$ (**3-II**)
M_r	389.05	522.44	332.95	332.95
crystal color	colorless	colorless	colorless	colorless
crystal size, mm	0.30 × 0.10 × 0.02	0.40 × 0.33 × 0.22	0.31 × 0.25 0.22	0.32 × 0.20 × 0.14
temperature, K	153 (2)	298 (2)	153 (2)	153 (2)
crystal system	triclinic	triclinic	triclinic	triclinic
space group (**Z**)	$P\bar{1}$ (**6**)	$P\bar{1}$ (**2**)	$P\bar{1}$ (**6**)	$P\bar{1}$ (**2**)
a, Å	7.2902(15)	6.810(3)	7.2778(12)	5.317 (3)
b, Å	8.3757(17)	9.037(4)	8.4129(14)	7.694(5)
c, Å	61.789(13)	25.214(11)	52.322(8)	24.809(15)
α, °	88.085(3)	92.057(8)	90.188(3)	92.633(10)
β °	89.908(3)	94.654(8)	92.688(4)	94.194(11)
γ, °	71.268(3)	108.591(7)	108.799(3)	101.821(11)
V, Å^3	3570.8(13)	1462.8(11)	3028.8(8)	988.8(11)
D_{calc} (g cm^{-3})	1.086	1.186	1.095	1.118
F(000)	1296	564	1104	368
μ(Mo Kα) (mm^{-1})	0.173	0.422	0.194	0.198
2θ range	5−46	2−50	1.5−50	2−57
reflections measured	25771	10896	14852	9454
unique reflections	10663	5128	10096	4378
wR2 (R1)	0.1745 (0.0612)	0.2118 (0.1046)	0.2579 (0.0793)	0.1392 (0.0466)

the bulk material in a mixture of toluene and $CHCl_3$ and storing the mixture at 4 °C for 30 d. Recrystallization of [C_{14}-mim]Cl from hot ethyl acetate provided crystals of **3-I** for X-ray diffraction studies. **3-II** was crystallized from 1,2-dichoroethane held at 50 °C for 48 h.

Experiment and crystal details are listed in Table 1. Data for **1** were collected on a Bruker SMART diffractometer at the SRS, Daresbury, U.K. on beamline 9.8.[25] Data for **2** were collected on a Siemens P4 diffractometer using the XSCANS software with omega scans. Data for **3-I** and **3-II** were collected on a Bruker SMART diffractometer using the SAINT-NT software. For **1**, **3-I**, and **3-II**, the crystal was mounted onto the diffractometer at low temperature under nitrogen at ca. 153 K. For **2** the sample was mounted onto the diffractometer at room temperature. The structures were solved using direct methods with the SHELXTL program package. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were added at idealized positions with a riding model and fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for methyl)). The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2\ |F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max\ |F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre contains relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

Results and Discussion

The structure of [C_{18}-mim]Cl·H_2O (**1**) is characterized by three main features: (1) strong hydrogen bonding interactions between the chloride ions and water molecules forming an O−H···Cl chain; (2) two different conformations of the imidazolium headgroups with respect to the C18 alkyl chains, i.e., linear and bent; and (3) ordered interdigitation of the bent and linear C18 alkyl chains resulting in a double bilayer, Figure 3. The ordered interdigitation of the C18 alkyl chains results in two separate regions of imidazolium headgroups, chloride ions, and water molecules with different hydrogen bonding motifs. First, the Cl^- and H_2O associated with the linear headgroups form a $\{[H_2O]Cl\}_2^{2-}$ square dimer. These squares are isolated from one another and hydrogen bond to the imidazolium headgroup through C−H···O and C−H···Cl interactions from the C4 and C5 carbons, respectively. The chloride ions are also involved in C−H hydrogen bonds from both the C2 and the methyl carbon atoms. In comparison, the bent imidazolium headgroups are associated with disordered Cl^- and H_2O molecules. Although this disorder complicates the interactions, the Cl^- and H_2O molecules also form the square arrangement but now the C2, C5, and C6 (alkyl chain) and C4 and C6 (alkyl chain) carbons form hydrogen bonds with the Cl^- and H_2O molecules, respectively. The relative inclinations of the imidazolium rings to the chains are seen from an examination of the C2−N1−C6−C7 torsion angles of 132.7° and −72.1° for linear and bent orientations, respectively.

The influence of the C2-chloride interactions on the crystal structures of the long-chain imidazolium salts was examined by replacing the C2 hydrogen with a methyl group, effectively blocking the possibility of hydrogen bonding interactions. Unlike **1,** the crystal structure of [C_{18}-dmim]Cl·H_2O·$CHCl_3$ (**2**) does not adopt the double bilayer motif and does not contain conformationally different imidazolium cations. Instead, the structure is made up of a single bilayer with the [C_{18}-dmim]$^+$ chains interdigitated and the imidazolium headgroups on either side of the bilayer involved in $\pi-\pi$ interactions, as shown in Figure 4. The $CHCl_3$ molecules are disordered and are associated with the headgroups and lie "within" the cationic bilayer. However, despite these differences the water molecules and chloride ions form the same square $\{[H_2O]Cl\}_2^{2-}$ dimer. The dimers are isolated from one another although there are close contacts with the disordered chloroform molecules. Furthermore, the hydrogen atoms attached to C4 and C5 form hydrogen bonds with the chloride ions. The methyl group on the N3 position of the imidazolium ring also makes close contacts with the chloride ions, whereas the C2 methyl group is involved in weak interactions with the disordered chloroform molecules. The relative inclination of the chains to the rings is essentially orthogonal (C2−N1−C6−C7 torsion angle of −81.3°) showing a similar arrangement to that found for the bent conformation in (**1**). This conformation is also observed in some short chain ($n \leq 8$) C(2) methyl-protected imidazolium salts such as [C_n-dmim][$PdCl_4$]

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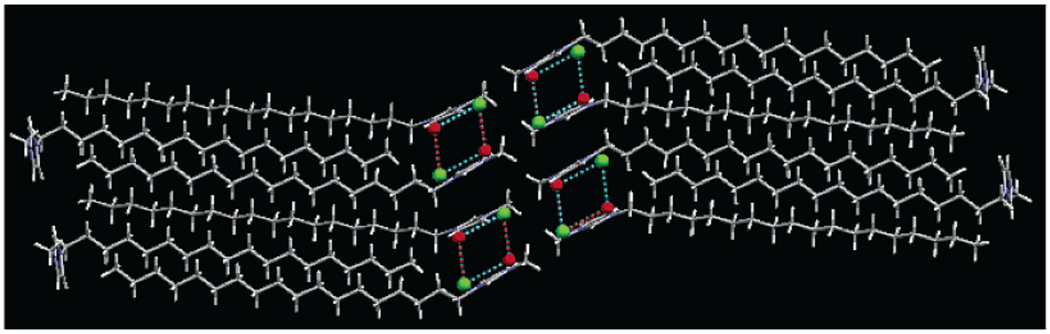

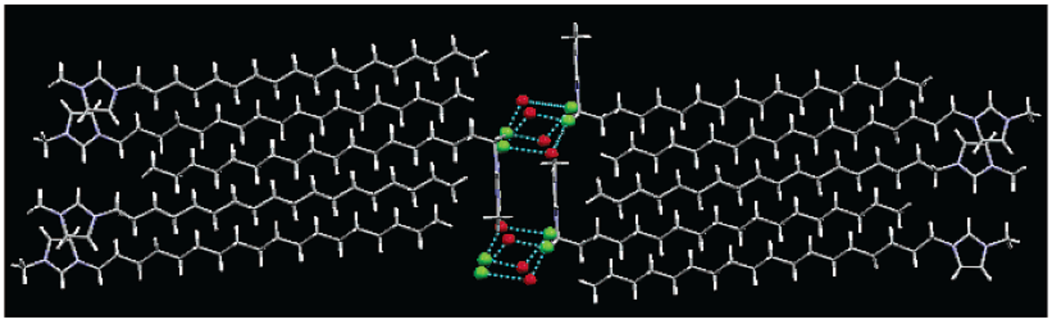

Figure 3. Two different regions in **1**: top is the linear headgroup region with the ordered O−H···Cl square dimers; bottom is the orthogonal headgroup with the disordered O−H···Cl square dimers. The dotted lines represent hydrogen bonds.

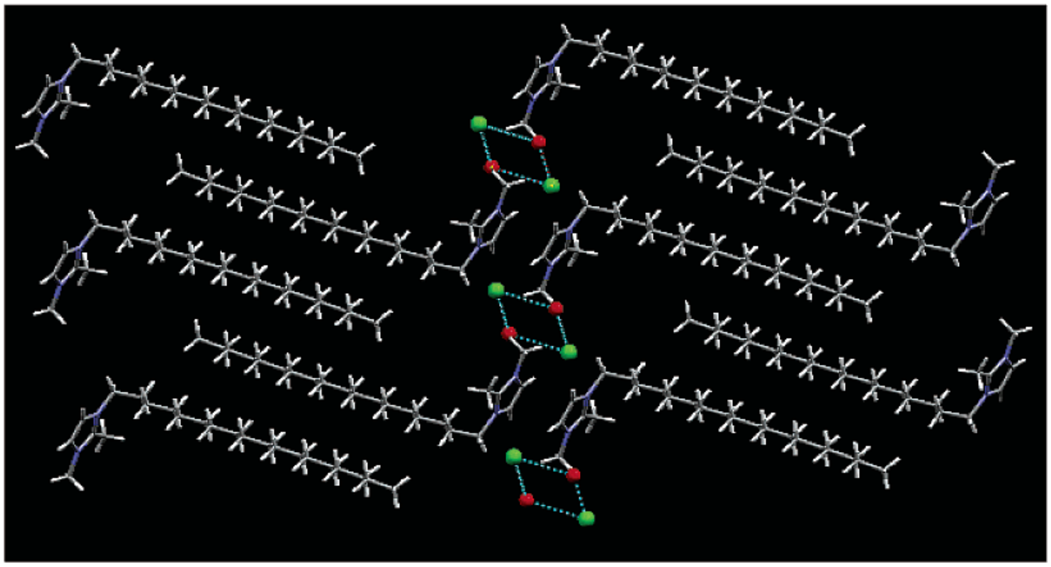

Figure 4. Packing diagram of **2** showing the interdigitated C_{18} chains and the O−H···Cl hydrogen-bonded dimer. The disordered $CHCl_3$ solvent molecules have been removed for clarity. The dotted lines represent hydrogen bonds.

(n = 5,6 and 8), [C_8-dmim][$PtCl_4$], [C_4-dmim][$CH_6B_{11}Cl_6$], and [C_3-dmim]Cl salts.[26] These observations suggest that C(2) methyl-protection of the imidazolium ring promotes a bent configuration for the alkyl chain relative to the imidazolium ring. This may be in part due to the fact that there are no longer any C(2) hydrogen-anion interactions or it may be due to steric hindrance from the methyl substituent.

Similarly to **1**, the crystal structure of **3-I** adopts a double bilayer architecture wherein interdigitated linear alkyl chain regions are bordered on either side by conformationally different imidazolium cations. Both regions contain $\{[H_2O]Cl\}_2^{2-}$ dimeric units as the dominant structural motif the same as that observed in **1**. The linear [C_{14}-mim]$^+$ cation region contains $\{[H_2O]Cl\}_2^{2-}$ square hydrogen-bonded dimers. The [C_{14}-mim]$^+$ cations form hydrogen bonds via C−H···O and C−H···Cl contacts utilizing the C4, C5, C2, and methyl carbons from the surrounding cations. Thus, each cation bridges two $\{[H_2O]Cl\}_2^{2-}$ units via three ring hydrogen atoms, while each $\{[H_2O]Cl\}_2^{2-}$ unit bridges four cations. This arrangement uses all the ring hydrogen atoms, necessitating only a slight inclination of the linear alkyl chain relative to the plane of the imidazo-

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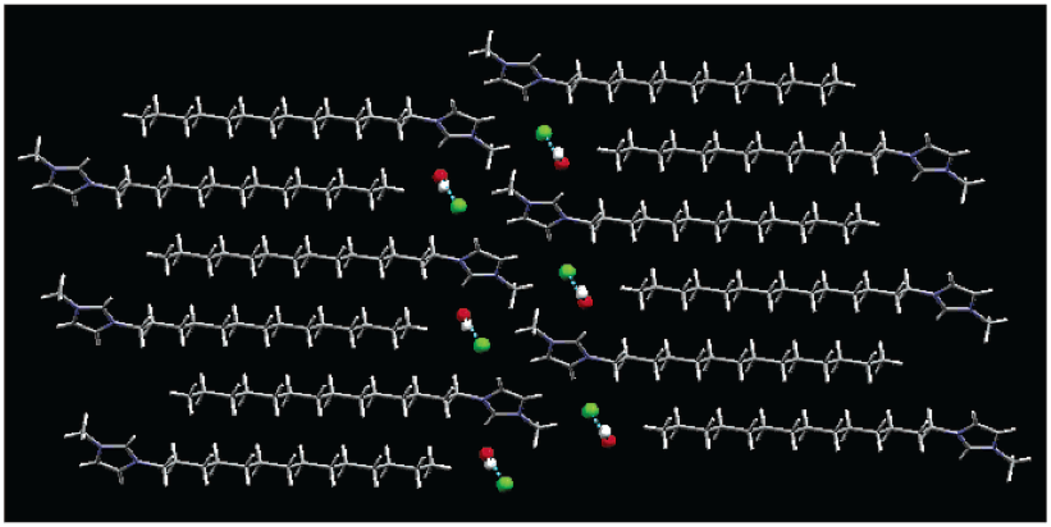

Figure 5. Packing diagram showing the interdigitated C_{14} chains of **3-II** with the hydrogen bonded O−H···Cl chains along the (001) direction. The dotted lines represent hydrogen bonds.

lium ring with an angle of 35° between the alkyl chains and headgroups. The hydrogen bonding observed in the alternate regions also involves $\{[H_2O]Cl\}_2^{2-}$ dimeric units, although the disorder among the water molecules and imidazolium headgroups makes interpretation difficult. However, the general features of the hydrogen bonding mimic those found in **1**. In this region the imidazolium headgroup is approximately orthogonal to the alkyl chain with an angle between the alkyl chains and headgroups of 89° and the imidazolium carbon atoms hydrogen bond to the $\{[H_2O]Cl\}_2^{2-}$ dimers.

The differences between **3-I** and **3-II** of $[C_{14}$-mim]Cl·H_2O arise from the orientation of the imidazolium headgroups and the hydrogen bonding between the chloride ions and the water molecules resulting in the formation of a single bilayer in **3-II** rather that the double bilayer seen in **1** and **3-I**. In each case, the $[C_{14}$-mim$]^+$ chains are interdigitated. Unlike **1** and **3-I** above there is no conformational variation between the headgroups in **3-II** and the cations all adopt a linear configuration. The Cl^- and H_2O molecules hydrogen bond with one another; however, they no longer form the square motif seen in **1**, **2**, and **3-I**. Instead of this, they form an infinite O−H···Cl hydrogen-bonded chain in the (010) direction, Figure 5. The cations form hydrogen bonds to these chains via C−H···O and C−H···Cl interactions from the C2 and C5 carbon atoms, respectively.

The structures described for **3-I** and **3-II** are consistent with the SAXS data which show a periodicity of 50.7 Å for the $[C_{14}$-mim]Cl·H_2O crystallized from 1,1,1 trichloroethane and 25.8 Å after cooling from the isotropic liquid. In our original report,[24] these changes in the SAXS were postulated to be due to a hydrated and a dehydrated phase, respectively; however, from the structures of **3-I** and **3-II** reported herein, these clearly suggest that this is not the case. These structures show that the two crystalline phases are, in fact, monohydrate polymorphs. These structural changes, as opposed to dehydration, indicate the origin of the large changes reported in the transition temperatures and enthalpies from DSC thermograms on the first versus second heating cycles.[24] For the $[C_{14}$-mim]Cl·H_2O, the transition temperature to the smectic A liquid crystalline phase occurred at 49.1 °C with a melting enthalpy of 41.6 kJ mol^{-1} on the first heating cycle, whereas on the second heating cycle the transition occurred at 19.4 °C with an enthalpy change of only 3.6 kJ mol^{-1}. Furthermore, on reexamining the DSC thermograms for **3-I** and **3-II**, the data show that similar changes in the peak temperatures and melting enthalpy are observed irrespective of whether the crystal is only melted into the mesophase without forming the isotropic liquid, i.e. to temperatures below 80 °C which is too low for dehydration to occur, or is heated past the clearing point. Examining the corresponding crystal structures, it is apparent that the major difference between the two polymorphs is the bent conformation of the double bilayer compared with the linear configuration of the conventional bilayer. Thus, the differences in the melting enthalpy are associated with the higher strain inherent in the bent compared to the linear conformation.

The strong tendency of water and halide ions to form hydrogen bonds explains why many halide-based ionic liquids readily absorb water from the atmosphere and often form monohydrate structures. We note, for example, that the $[C_8$-mim]Cl absorbs approximately 6% (w/w) under ambient conditions over 2.5 h,[11b] which roughly corresponds to a 1:1 mixture of $[C_8$-mim]Cl and water. Hydrogen bonding interactions between imidazolium ionic liquids and water have also been suggested to play an important role in density trends for ionic liquid mixtures.[11b] We also note that the architectures of these crystal structures correlate well with the results observed by Cammarata et al.[27] for liquid imidazolium salts that have been allowed to absorb water under ambient conditions. They concluded that “the anions play a major role in the solubility and miscibility of water with room-temperature ionic liquids, while the cations probably play a secondary role”, and that “the preferred sites of interaction with water molecules are the anions.”

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Only two crystal structures of a long-chain $[C_n\text{-mim}]^+$ or $[C_n\text{-dmim}]^+$ salt have been published, namely $[C_{12}\text{-mim}][PF_6]$ and $[C_{14}\text{-mim}][PF_6]$.[18,19] We have also been able to crystallize some other long-chain imidazolium salts in our laboratories, namely $\{[C_{12}\text{-mim}]_2[UO_2(NO_3)_4]\}$ and $\{[C_{16}\text{-mim}]_2[(UO_2)_2(NO_3)_4\ (C_2O_2)]\}\cdot 5CH_3CN$.[28] Interestingly these salts do not contain any water within their structure and none exhibit the double bilayer structure seen in **1** and **3-I** above. This observation from the extant single-crystal data is also borne out by the SAXS data for the $[C_n\text{-mim}]^+$ salts of trifluoromethanesulfonate, bis(trifluoromethanesulfonyl)imide, and tetrafluoroborate,[24] all of which exhibit the single bilayer behavior and also have no bound water. From these observations it would seem that the presence of water is a major factor in the thermal polymorphism of the $[C_n\text{-mim}]X$ ($n = 12-20$, X = Cl, Br) materials.

The $\{[H_2O]Cl\}_2^{2-}$ dimer is a common feature of hydrated halide salts and is also present in $[C_2\text{-dmim}]Cl\cdot H_2O$.[16] Furthermore, a comparison of the structures **1**, **2**, and **3-I** shows that substitution of the C2 position with a methyl group does not affect the formation of the $\{[H_2O]Cl\}_2^{2-}$ dimer motif in **2**, but may promote a bent configuration versus a linear configuration. The effect of the $CHCl_3$ molecules in this structure is not clear. However, it is possible that the extra bulk of the $CHCl_3$ solvent may reduce the conformational flexibility of the alkyl chains relative to the headgroups. This “bulk” effect may be a further reason that the double bilayer motif is not observed for imidazolium salts containing other anions or solvent molecules. For example, in $[C_{14}\text{-mim}][PF_6]$[19] the alkyl chains are bent near the headgroup, adopting a “spoon-shaped structure”[15] in order to accommodate the anion. The linearity of the alkyl chains in these and similar systems (*N*-alkylpyridinium salts pack in the same manner[29]) consistently results from interdigitated molecular packing. The orientation of the chains with respect to the headgroup may depend on the anion, substitution of the imidazolium ring, and the presence of solvent molecule in the lattice. Furthermore, a search of the CSD for quarternary-amonium, alkylpyridinium, and bis-alkyl-benzimidazolium hydrated halide salts revealed 13 structures.[30] All of these structures except one (dodecyl-dimethyl-propylammonium bromide hemihydrate[31]) contain either the square $\{[H_2O]Cl\}_2^{2-}$ dimer as in **3-I** or the $[H_2O]Cl^-$ chains as in **3-II**. The exception to these two motifs forms an isolated $\{[H_2O]Br\}_2^{2-}$ motif, which is probably due to the fact that it is a hemihydrate rather that a monohydrate.

Thermal polymorphism is not uncommon in long-chain imidazolium salts. For example, crystal polymorphism was observed in 1-alkyl-3-methylimidazolium tetrachloropalladate(II) salts ($[C_n\text{-mim}]_2[PdCl_4]$, $n = 10-18$).[32] Here, up to three separate crystal phases were noted, as well as the mesophase and isotropic liquid with the first heating cycle showing irreversible behavior, as shown for the 1-alkyl-3-methylimidazolium halide salts.[24] For heating cycles thereafter, reversible behavior was observed without the first crystal−crystal transition. However, to date, the individual crystal structures have not been determined.

Conclusions

The thermal behavior of long-chain 1-alkyl-3-methylimidazolium salts with chloride anions has been studied using single-crystal X-ray diffraction. This study has shown that our initial supposition that the thermal history dependence of the crystalline phases before and after melting is indeed due to conformational variations in the imidazolium headgroups.

Furthermore, the solid state architectures of these solvated, long-chain imidazolium chlorides consist of regions containing interdigitated linear alkyl chains, alternating with regions containing imidazolium headgroups, chloride ions, and solvent. The nature of these layers, particularly the incorporation of water molecules via complex hydrogen-bonding interactions, may help to explain the persistent presence of water in imidazolium ionic liquids. It seems likely that the strong O−H···Cl hydrogen bonds in these compounds may be the reason that they are not easily dehydrated. It also seems likely that the effect of substitution on the C(2) position of the imidazolium ring is to inhibit the “linear” conformation of the alkyl chains. However, it is not clear whether this is due to the inability of the methyl substituent to form hydrogen bonds or the added steric bulk associated with the methyl group in this position. A comparison of the hydrates of the related long-chain quarternary-amonium, alkylpyridinium, and bis-alkyl-benzimidazolium hydrated halide salts exhibit the same halide water hydrogen-bonding motifs as those found for the imidazolium salts. Further investigation of the factors affecting the behavior of these hydrated halide salts will require the crystallographic characterization of a wider range of long chain salts. This research is ongoing in our laboratory.

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Supporting Information Available: X-ray crystallographic information files (CIF) are available for $[C_{18}\text{-mim}]Cl\cdot H_2O$ (**1**), $[C_{18}\text{-dmim}]Cl\cdot H_2O\cdot CHCl_3$ (**2**), and $[C_{14}\text{-mim}]Cl\cdot H_2O$ (**3-I** and **3-II**). This information is available free of charge via the Internet at http://pubs.acs.org.

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