Received: October 22, 2013 | Accepted: November 19, 2013 | Web Released: November 23, 2013 CL-130982

Crystal Structure of 1,3-Dimethylimidazolium Bis(fluorosulfonyl)amide: Unexpectedly High Melting Point Arising from Polydentate Hydrogen Bonding

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1,3-Dimethylimidazolium bis(fluorosulfonyl)amide, [C$_1$mim]FSA, is an ionic liquid with a lower viscosity than the bis(trifluoromethanesulfonyl)amide salt, [C$_1$mim]NTf$_2$, but with a higher melting point. The single-crystal X-ray structure analysis reveals that this is because the [C$_1$mim]FSA crystal has low coordination ion number and three types of highly symmetric polydentate C–H···O hydrogen bonds.

Room-temperature ionic liquids (RTILs) are a new class of liquids that have attracted a lot of attention because of their interesting and characteristic properties.[1,2] It is crucial that general correlation between the structure and physicochemical properties is clarified so that this can be achieved. For example, it has been demonstrated that the variety of conformation of the molecular ion plays an important role to obtain RTILs with low melting point.[3] Many studies have been focused on the way how varieties and flexibilities of alkyl chain conformations in cations relate to the physicochemical properties, and it has been shown that the flexibility of the RTIL cation strongly affects the phase-transition behavior, thermal properties, structure, and dynamics.[3,4] In this way, there have been many studies focused on RTIL cations.

We are now interested in the relationship between the physicochemical properties and the anion structures. Bis(fluorosulfonyl)amide and bis(trifluoromethanesulfonyl)amide (abbreviated to [FSA]$^-$ and [NTf$_2$]$^-$, respectively), which are typical RTIL anions, contain two stable rotamers with a small energy difference.[5,6] A number of crystal structure analyses[7] and theoretical and spectroscopic studies[8] have been performed on the imidazolium-based NTf$_2$ salts, whereas the number of structure studies on the FSA salts is limited.[9,10] Comparing the structures and physicochemical properties of the two anions will provide useful information. We synthesized 1,3-dimethylimidazolium bis(fluorosulfonyl)amide ([C$_1$mim]FSA) (Figure 1) and measured its viscosity and melting point, preformed single-crystal X-ray analysis, and compared its structural characteristics with those of [C$_1$mim]NTf$_2$.[7b]

The salts [C$_1$mim]FSA and [C$_1$mim]NTf$_2$ were synthesized following a previously established procedure,[2] as described in the Supporting Information.[11] Calorimetric measurements were conducted from 213 to 353 K at a scanning rate of 5 mK s^{-1} using a laboratory-made calorimeter.[12] The crystal–liquid phase transition for each salt was visually determined using a Linkam TMS94 temperature-controlled stage, and the melting point was taken to be the endothermic peak maximum. The viscosities of the two salts were measured using an Anton Paar AMVn viscometer at 333 K because the liquid [C$_1$mim]FSA crystallized immediately below its melting point (331 K) in the glass capillary cell. [C$_1$mim]FSA single-crystals were obtained by recrystallization from methanol. X-ray diffraction data were collected at 173 K.

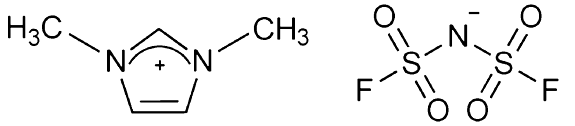

Figure 1. Structure of 1,3-dimethylimidazolium bis(fluorosulfonyl)amide ([C$_1$mim]FSA).

Melting points and viscosities of [C$_1$mim]FSA and [C$_1$mim]NTf$_2$ are listed in Table 1, and those of the corresponding [C$_2$mim]$^+$ salts are included for comparison.[13] Each [FSA]$^-$ salt was less viscous than the corresponding [NTf$_2$]$^-$ salt, which could probably be attributed to the lower molecular weight and weaker nucleophilicity of bis(sulfonyl)amide group in [FSA]$^-$ than that in [NTf$_2$]$^-$, because the fluoro group is more electronegative than the CF$_3$ group.[14] Melting points of both of the [C$_2$mim] salts were almost the same, but the [C$_1$mim]FSA melting point was markedly higher than that of [C$_1$mim]NTf$_2$, which is difficult to explain considering molecular weights, electrostatic interactions, and conformational variations. A characteristic cation–anion interaction geometry might be speculated to exist in the [C$_1$mim]FSA; therefore, we attempted to investigate this possibility by performing single-crystal X-ray diffraction analysis.

The [C$_1$mim]FSA salt crystallized in the orthorhombic *Pbcm* space group. The detailed crystal structure data are presented in Table S1 in the Supporting Information.[11] As shown in Figure 2, both the cation and anion form a completely symmetric structure, with the C1 and H1 of the cation and N2 of the anion located on the crystallographic mirror plane. The [FSA]$^-$ conformation was observed to be perfectly *cisoid* with F–S–N–S torsion angles of ±74.1(1)°. On the other hand, if [NTf$_2$]$^-$ would form a completely symmetric cisoid conformer, it would be unstable because of steric effects involving the two bulky CF$_3$ groups. To the best of our knowledge, a perfectly *cisoid* conformation of a bis(sulfonyl)amide-based anion has never been found in other salts.

The characteristic structure unit shown in Figure 2 indicates that the crystal has a bilaterally symmetric cation–anion

Table 1. Melting point and viscosity of various ionic liquids

Anion	[C$_1$mim]$^+$		[C$_2$mim]$^+$	
	T_m/K	η^a/mPa s	T_m/K	η^b/mPa s
[FSA]$^-$	331.0	8.2	260.1^c	24.5^c
[NTf$_2$]$^-$	298.5	13.2	256.8^c	45.9^c

^{a}At 333 K. ^{b}At 298 K. ^{c}ref 13.

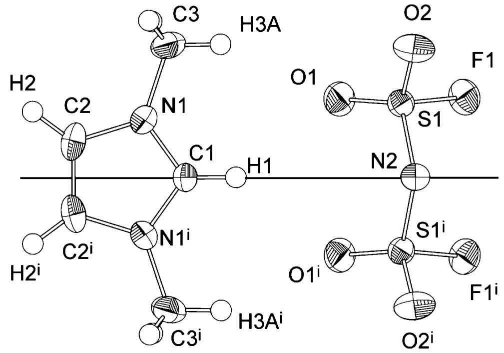

Figure 2. Asymmetric unit with symmetry equivalent atoms (symmetry operation: (i) $x, y, 1/2 - z$) of [C_1mim]FSA with 50% ellipsoidal probability. The solid line indicates the crystallographic mirror plane.

Table 2. Hydrogen bonding in the crystal of [C_1mim]FSA[a]

C–H···O	$d_{\mathrm{H\cdots O}}$ /Å	$d_{\mathrm{H\cdots O}}$ − vdW[b] /Å	$d_{\mathrm{C\cdots O}}$ /Å	$\angle_{\mathrm{C\text{–}H\cdots O}}$ /°
C1–H1···O1	2.43	−0.29	3.242(2)	143
C3–H3A···O1	2.45	−0.27	3.362(2)	154
C2–H2···$O2^{ii}$	2.55	−0.17	3.491(2)	169
C3–H3C···$O2^{iii}$	2.63	−0.09	3.442(2)	141

[a]Symmetry operations: (ii) $2 - x$, $1/2 + y$, z; (iii) $1 - x$, $1/2 + y$, z. [b]vdW: sum of the van der Waals radii.

interaction geometry. We used the Bondi van der Waals radii as atomic radii,[15] and studied the interactions between the cations and anions in the crystal.

All of the cation–anion interactions in [C_1mim]FSA were found to involve C–H···O hydrogen bonds, and are summarized in Table 2. The fluoro group in the [FSA]$^-$ did not interact with the cation. It is well-known that strong interactions can be formed by the hydrogen atom at the 2-position of the imidazolium ring.[7,16] In the studied crystal, the H1···O1 and H3A···O1 interatomic distances were significantly shorter than the sum of van der Waals radii, indicating strong interactions. H1 is the hydrogen atom at the 2-position of the imidazolium ring. The mirror symmetry operation of the asymmetric unit revealed the presence of characteristic W-shaped tridentate hydrogen bonding (Figure 3a), which is typically observed in 1,3-dialkylimidazolium-based NTf_2 salts.[7b,7d,7e]

In-plane hydrogen bonding was also observed around the 4- and 5-positions of the imidazolium ring, forming bidentate hydrogen bonding (Table 2 and Figure 3a). In-plane interactions were formed by a single [C_1mim]$^+$ and two [FSA]$^-$, and vice versa. However, bidentate hydrogen bonding at the 4- and 5-positions was not found in [C_1mim]NTf_2, and each H atom interacted with a different [NTf_2]$^-$. The in-plane hydrogen bonding showed that three [NTf_2]$^-$ surrounded [C_1mim]$^+$[7b] (Figure S3 in the Supporting Information).[11] We believe that the lower coordination ion number in [C_1mim]FSA than in the [C_1mim]NTf_2 leads to stronger cation–anion interactions and plays an important role in [C_1mim]FSA having a higher melting point.

The anion above the imidazolium plane (at the symmetry position (iii) $1 - x$, $1/2 + y$, z and (v) $1 - x$, $1/2 + y$, $1/2 - z$) formed the relatively weak bidentate hydrogen bonds H3C···$O2^{iii}$ and H3C^{i}···$O2^{v}$ (Figure 3b).

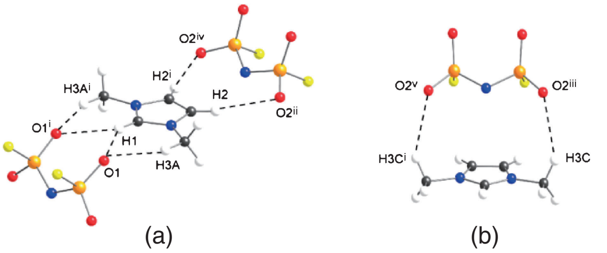

Figure 3. (a) In-plane hydrogen bonding and (b) out-of-plane hydrogen bonding in a [C_1mim]FSA crystal. Grey: carbon, blue: nitrogen, yellow: fluorine, orange: sulfur, red: oxygen, and white: hydrogen. Symmetry operations: (iv) $2 - x$, $1/2 + y$, $1/2 - z$; (v) $1 - x$, $1/2 + y$, $1/2 - z$.

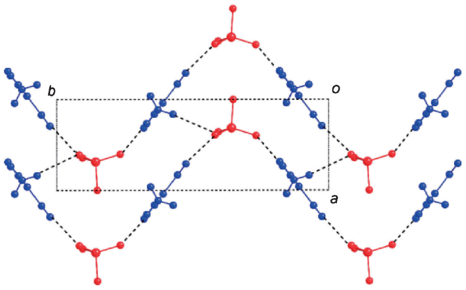

Figure 4. Hydrogen-bonded undulating chain structure of [C_1mim]FSA projected along the c axis ($z = 0$–$1/2$). Blue: cation and red: anion.

Differently from the [C_1mim]NTf_2 crystal, all the cation–anion interactions in the [C_1mim]FSA crystal could be characterized by polydentate hydrogen bonding (Figure 3). This is the cause for the unexpectedly high melting point of the [C_1mim]FSA crystal, because the highly symmetric polydentate interactions will strongly inhibit rotation around the S–N–S bonds and decrease the flexibility of the anion in the crystal.

A packing diagram for [C_1mim]FSA is shown in Figure 4. Successive in-plane interactions along the b axis result in an undulating chain structure. Concomitantly, out-of-plane hydrogen bonding between the H3C and $O2^{iii}$ contributes to a stack of chains along the a axis. There are no cation–anion interactions along c axis (Figure S4 in the Supporting Information).[11]

In conclusion, in spite of the fact that the [C_1mim]FSA liquid has a low viscosity compared with the [C_1mim]NTf_2 liquid, the former salt has an unexpectedly high melting point. [C_1mim]FSA crystal structure revealed a low coordination ion number and a perfectly symmetric polydentate hydrogen bonding. The rigid packing structure contributed to its higher melting point than the related salts. In the future, we intend to study the flexibility and dynamics of salts containing the amide-anion to elucidate the relationship between conformation and properties.

This study was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [for K. N., No. 21245003 Grant-in-Aid for Scientific Research (A)]. The authors thank Dr. T. Mandai for his experimental support.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Experimental details and Crystallographic data in CIF(CCDC 963540).

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