



TITLE:

Coordination environment around the lithium cation in solid Li(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)) (EMIm=1-ethyl-3-methylimidazolium): Structural clue of ionic liquid electrolytes for lithium batteries

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## Coordination environment around the lithium cation in solid

$\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  (EMIm=1-ethyl-3-methylimidazolium):

## Structural clue of ionic liquid electrolytes for lithium batteries

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*Key words:* ionic liquid, lithium battery, room temperature molten salt, room temperature ionic liquid, bis(trifluoromethylsulfonyl)amide, structure

**ABSTRACT.**

Crystal structure of  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  (EMIm = 1-ethyl-3-methylimidazolium cation) has been determined by single-crystal X-ray diffraction as a structural clue of ionic liquid electrolytes for lithium batteries.  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  crystallizes in the space group  $P2_1/c$ ,  $a = 15.184(3)$  Å,  $b = 11.358(3)$  Å,  $c = 21.249(5)$  Å,  $\beta = 111.454(12)^\circ$ ,  $Z = 4$ ,  $V = 3561.18(14)$  Å<sup>3</sup>. Two of the three  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anions have *cis*-conformations and the third anion shows a *trans*-conformation. The asymmetric unit contains two crystallographically independent lithium ions and both of them are trigonal-bipyramidally coordinated by five oxygen atoms of  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anions, forming a two-dimensional network. EMIm cation occupies a space in the network, weakly interacting with the anions.

## 1. Introduction

Ion-ion and ion-molecular interaction in solutions have been interesting themes for electrochemists since they are crucial for designing functional electrolytes. Solution of a lithium salt is one of the important examples because the small ionic radius of  $\text{Li}^+$  yields various unique coordination environments around it. Moreover, the application of lithium salts as electrolytes for lithium batteries has promoted research on this subject. Theoretical and computational approaches to determining structures of solutions of lithium salts are current topics of interest, with most studies being devoted to the ion-pair formation that reduces the number of charge carriers in the electrolyte.  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (lithium bis(trifluoromethylsulfonyl)amide, LiTFSI), developed by Armand and his coworkers, exhibits excellent properties as a supporting electrolyte dissolved in organic solvent or impregnated in polymer owing to its flexible and charge-delocalized anion [1]. A number of studies have been carried out to elucidate the coordination environment around  $\text{Li}^+$  in the solution of  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  [2-8]. A solid-state structural approach has also been commonly used, since local interaction in a lattice provides preliminary insights to understanding the liquid structure [9, 10].

The unique properties of room temperature ionic liquids (often called room temperature molten salts), such as non-volatility, non-flammability and a wide liquid-phase temperature range, have attracted much attention in view of potential applications in synthetic chemistry and electrochemistry [11-21]. Especially, the application of these ionic liquids in lithium batteries has been examined to improve their safety taking advantage of their non-flammability.  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  is widely used in this field since it gives salts with low melting points combined with wide variety of cations [22-24]. In the present study, we have focused on the most typical combination,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ -EMIm $\text{N}(\text{SO}_2\text{CF}_3)_2$ , as a model for a room temperature ionic liquid electrolyte for a lithium battery (Fig. 1) [25-27]. Here we report the structure of  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  and discuss the coordination environments around Li ions.

## 2. Experimental

### 2.1 Synthesis

$\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (Morita Chemical Industries, purity > 99.0 %) was used as supplied. Acetonitrile (Wako Pure Chemical Industries, purity 99 % and water content < 50 ppm) and ethyl acetate (Wako Pure Chemical Industries, purity 99 % and water content < 50 ppm) were used as purchased. EMImCl (Sanko Chemical Industries, purity 98.5 %) was recrystallized from acetonitrile solution by adding ethyl acetate and dried under vacuum ( $\sim 1$  Pa) at 343 K for one week. EMImN( $\text{SO}_2\text{CF}_3$ )<sub>2</sub> was prepared by the reaction of EMImCl and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  in distilled water. Obtained EMImN( $\text{SO}_2\text{CF}_3$ )<sub>2</sub> was washed by distilled water several times and dried under vacuum ( $\sim 1$  Pa) at 400 K for three days.

### 2.2 Crystal growth

Single crystals of  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  were grown from  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ -EMImN( $\text{SO}_2\text{CF}_3$ )<sub>2</sub> mixture under the condition of a slight excess of EMImN( $\text{SO}_2\text{CF}_3$ )<sub>2</sub> from its stoichiometric ratio. The mixture in a reaction tube was heated up to around 373 K, yielding a solution with a small amount of solid phase, and was then slowly cooled down to room temperature. After this treatment was repeated a few times, the sample was kept at room temperature for a week. Once the whole part of the mixture was melted, it was kept in a supercooled state and no precipitation occurred even after one week.

### 2.3 X-ray crystallography

X-ray diffraction data were collected at 298 K using Nonius KappaCCD diffractometer with a CCD area detector and monochromated Mo-K $\alpha$  radiation. The single crystal fixed in a quartz capillary under argon atmosphere was mounted on a goniometer head. The obtained data were processed by the program DENZO-SMN [28]. The program SORTAV was used for the absorption correction [29]. The SHELX-97 suite of programs were used for the solution and refinement of the structure [30]. All the non-hydrogen atoms were determined by the direct method and difference Fourier synthesis by introducing anisotropic displacement parameters. All the hydrogen atoms were

refined using appropriate riding models, with C-H distances of 0.97 Å for CH<sub>2</sub>, 0.96 Å for CH<sub>3</sub> and 0.93 Å for aromatic groups. The displacement parameters of H atoms were fixed at 1.2  $U_{eq}$  of their parent atoms (1.5  $U_{eq}$  for methyl groups).

### 3. Results and discussions

Structural data for Li<sub>2</sub>(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> are given in Table 1. Thermal ellipsoid plots of the ions in the Li<sub>2</sub>(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> asymmetric unit are shown in Fig. 2. Selected bond lengths and angles for EMIm cation and N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> anions in Li<sub>2</sub>(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> are given in Table 2 and 3, respectively. For EMIm<sup>+</sup>, the position of the β-carbon in the ethyl group, C(47), which sticks out of the plane of the imidazolium five-membered ring (torsion angle of 66.5(8)°), is not determined well due to its high freedom in the space around it, resulting in a large displacement factor. Two of the three N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> anions have *cis*-conformations (C-S...S-C torsion angles of 11.6(8)° for anion (1) and 15.6(8)° for anion (2)) and the third anion shows a *trans*-conformation (C-S...S-C torsion angle of 149.0(10)°). As discussed in the previous study, the *cis*-conformation of N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> has a higher energy than the *trans*- and is generally found in strong coordination environments such as in alkaline metal salts [31-33]. Li<sup>+</sup> has a strong coordination field also in the title structure resulting in the *cis*-conformation for some of the coordinating N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup>.

The coordination environments around two crystallographically distinct Li cations in Li<sub>2</sub>(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> are shown in Fig. 3 (a) and (b). Li-O bond geometries are given in Table 4. Both the Li cations are trigonal-bipyramidally coordinated by the five oxygen atoms of the anions, and no coordination by other atoms such as nitrogen is observed. Five Li-O bonds around Li(1) exhibit similar contact distances (1.95-2.08 Å), these values being similar to the observed distances in the LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> crystal (1.95(1) and 1.97(1) Å) [9]. Li(1) is located precisely on the equatorial plane (O(13)-O(14)-O(33)-Li(1) torsion angle of 0.1°) and the three O<sub>eq</sub>-Li(1)-O<sub>eq</sub> angles in the equatorial plane are 111.3(4)°, 122.1(5)° and 126.6(5)°. The five oxygen atoms are provided from three anions, i.e., two anions have bidentate coordination (O(11)--O(13) of *cis*-N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> (1) and O(31)--O(33) of *trans*-N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> in Fig. 2). In the case of Li(2), three oxygen atoms in the equatorial plane have shorter contact distances of less than 2 Å than the other two axial oxygen

atoms, and these bonds, Li(2)-O(22), Li(2)-O(23) and Li(2)-O(32), are somewhat bent toward the O(21) side to elongate the Li(2)-O(21) bond (2.350(11) Å) compared to Li(2)-O(12) (2.088(10) Å). The O(21)-Li(2)-O(12) angle is also bent toward the space between the O(23) and O(32), which is the widest of the three angles on the equatorial plane (130.2(5)° for O(23)-Li(2)-O(32), 112.2(5)° for O(22)-Li(2)-O(32) and 115.1(5)° for O(22)-Li(2)-O(23)). Only two oxygen atoms, O(21) and O(23), belong to the same anion (*cis*-N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> (2) in Fig. 2) and the other three oxygen atoms are in a monodentate coordination condition.

In both the cases of Li(1) and Li(2), bidentate coordination by two oxygen atoms on the same sulfur atom in the anion does not occur, only the two oxygen atoms bound to different sulfur atoms on the anion coordinating to the lithium atom in bidentate conditions that forces two of the three N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> anions to have energetically unfavorable *cis*-conformation. Both the conformations are also found for the anions having monodentate coordination to the lithium atoms. The complicated Li...O local interactions construct a two-dimensional network and EMIm<sup>+</sup> occupies a space in the network structure, weakly interacting with the anion. The distance between H(42) and O(34) of 2.65 Å is almost the same as the sum of the van der Waals radii for hydrogen and oxygen atoms forming a weak bond [34]. One hydrogen atom, H(46b), is detected to be involved in strong hydrogen bonding (2.32 Å for H(46b)-O(24)) in the title structure. Figure 4 shows a perspective view of the Li<sub>2</sub>(EMIm)(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> structure from the *b*-axis direction. This structure is regarded as a layered structure stacking from the upper left to the lower right in Fig. 4, similar to some other alkali metal salts of N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> [31]. As a result of Li<sup>+</sup>-N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> interactions described above, fluorine atoms on the -CF<sub>3</sub> group denoted by large circles in Fig. 4 are oriented to the surfaces of the layers to face each other forming a so-called fluorous region [33].

Results of computational studies on the Li<sup>+</sup>-N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> ion pair indicates that the coordination states by oxygen atoms are at lower energy levels than those including the nitrogen atom in spite of a larger negative charge on the nitrogen atom (approximately one and half times) than that on the oxygen atoms in a free environment [2,4-6,8]. Another computational study suggests that the coordination by the nitrogen atom becomes predominant in the case of larger metal cation [35], which agrees with the fact that the coordination by nitrogen atom is observed only in CsN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>

in a series of  $MN(SO_2CF_3)_2$  ( $M$  = alkaline metal) and their solvated crystals [31, 32]. Although the fluorine atom in the  $-CF_3$  group is also a candidate for  $Li^+$  to interact with, a lower negative charge than those on nitrogen and oxygen atoms reduces its possibility. Considering these results in addition to the present results on the solid-state structure of  $Li_2(EMIm)(N(SO_2CF_3)_2)_3$ , it is concluded that in room temperature ionic liquid electrolytes prepared by dissolving  $LiN(SO_2CF_3)_2$  in  $EMImN(SO_2CF_3)_2$ ,  $Li^+$  is expected to interact with  $N(SO_2CF_3)_2^-$  via oxygen atoms rather than nitrogen atoms or the  $-CF_3$  group.  $EMIm^+$  weakly interacts with the anion in the solution. A decrease in the concentration of the lithium salt from that for  $Li_2(EMIm)(N(SO_2CF_3)_2)_3$  would make the cation-anion interaction weaker to yield a liquid phase and enhance ion mobilities.

#### 4. Conclusion

$Li_2(EMIm)(N(SO_2CF_3)_2)_3$  was structurally characterized to obtain preliminary insights to liquid structures of ionic liquid electrolytes for lithium batteries. In  $Li_2(EMIm)(N(SO_2CF_3)_2)_3$ ,  $N(SO_2CF_3)_2^-$  have both *trans*- and *cis*- conformations. Lithium cations are trigonal-bipyramidally coordinated by five oxygen atoms of  $N(SO_2CF_3)_2$  anions containing bidentate coordinations, whereas  $EMIm$  cation weakly interacts with the anions. Li-O interactions observed in the  $Li_2(EMIm)(N(SO_2CF_3)_2)_3$  lattice agrees with the previously reported computational results about the coordination environment around lithium ion in lithium battery electrolyte that indicates O atoms predominantly interact with a Li cation than N atoms.

#### Supplementary materials

The supplementary material has been sent to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material No. 267312 and can be obtained by contacting the CCDC.

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## Figure captions

Fig. 1 Structures of (a) EMIm cation and (b)  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anion.

Fig. 2 Thermal ellipsoid plot of the individual ions in the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  asymmetric unit with atom numbering scheme. Li cations are drawn with the *cis*- conformation  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anions and H atoms are drawn as small circles of arbitrary radii.

Fig. 3 Coordination environment around  $\text{Li}^+$  in the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  structure for (a) Li(1) and (b) Li(2). The anion is drawn in a stick model except for oxygen atoms that link to  $\text{Li}^+$ .

Fig. 4 Perspective view of the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  structure from the *b*-axis. Large circles denote fluorine atoms. Li-O bonds are drawn in solid lines and H atoms are omitted for clarity.

Table 1 Structural data for  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$ 

Formula	$\text{C}_{12}\text{H}_{11}\text{F}_{18}\text{Li}_2\text{N}_5\text{O}_{12}\text{S}_6$
Molecular weight ( $\text{g mol}^{-1}$ )	965.50
Temperature (K)	298
Crystal system	Monoclinic
Space group	$P2_1/c$
Diffractometer	Nonius KappaCCD
$a$ (Å)	15.184(3)
$b$ (Å)	11.358(3)
$c$ (Å)	21.249(5)
$\beta$ (°)	111.454(12)
$V$ (Å <sup>3</sup> )	3561.18(14)
$Z$	4
Radiation	Mo $K\alpha$ (0.71073 Å)
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.801
$\mu$ ( $\text{mm}^{-1}$ )	0.536
$R1$ <sup>a</sup> ( $I > 2\sigma(I)$ )	0.0571
$wR2$ <sup>b</sup> ( $I > 2\sigma(I)$ )	0.1514
<sup>a</sup> $R1 = \sum   F_o  -  F_c   / \sum  F_o $ . <sup>b</sup> $wR2 = [\sum w[ F_o ^2 -  F_c ^2]^2 / \sum w F_o ^2]^{1/2}$	

Table 2 Selected bond lengths and angles for EMIm cation in  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  (Å, °)

N(41)-C(42)	1.298(10)	C(42)-N(43)	1.274(10)
N(43)-C(44)	1.432(12)	C(44)-C(45)	1.290(14)
C(45)-N(41)	1.286(12)	N(41)-C(46)	1.43(2)
C(46)-C(47)	1.10(3)	N(43)-C(48)	1.539(12)
N(41)-C(42)-N(43)	110.8(8)	C(42)-N(43)-C(44)	103.5(9)
N(43)-C(44)-C(45)	107.7(10)	C(44)-C(45)-N(41)	107.6(12)
C(42)-N(41)-C(45)	110.4(10)	C(42)-N(41)-C(46)	127.0(11)
C(45)-N(41)-C(46)	122.5(13)	N(41)-C(46)-C(47)	113(2)
C(42)-N(43)-C(48)	125.7(9)	C(44)-N(43)-C(48)	130.0(11)
C(42)-N(41)-C(46)- C(47)	66.5(8)		

Table 3 Selected bond lengths and angles for  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  anions in  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$ 

(Å, °)

	<i>cis</i> - $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ (1)	<i>cis</i> - $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ (2)	<i>trans</i> - $\text{N}(\text{SO}_2\text{CF}_3)_2^-$
S-N	1.563(4), 1.559(4)	1.578(6), 1.510(6)	1.535(8), 1.543(8)
S-O	1.414(3), 1.413(4) 1.421(4), 1.428(3)	1.462(4), 1.413(4) 1.424(4), 1.446(6)	1.423(4), 1.405(4) 1.401(6), 1.425(5)
S-C	1.819(7), 1.866(7)	1.860(8), 1.765(13)	1.853(9), 1.863(12)
C-F	1.297(8), 1.310(7) 1.322(7), 1.301(8) 1.264(8), 1.308(8)	1.322(9), 1.236(9) 1.282(8), 1.251(13) 1.275(12), 1.337(15)	1.296(11), 1.285(9) 1.279(9), 1.280(13) 1.287(16), 1.248(15)
S-N-S	126.4(3)	125.2(3)	127.4(4)
N-S-O	116.1(2), 110.8(2) 109.5(2), 115.8(2)	114.4(3), 112.2(3) 119.1(3), 106.2(4)	116.5(3), 110.1(4) 115.7(3), 111.6(5)
N-S-C	102.6(3), 104.2(3)	105.8(4), 106.1(5)	103.5(5), 98.5(7)
O-S-O	116.3(2), 117.0(2)	115.8(3), 116.5(4)	117.3(3), 118.7(4)
O-S-C	105.8(3), 103.2(3) 105.3(3), 103.3(3)	104.8(4), 102.0(3) 105.8(6), 101.2(7)	104.5(4), 102.8(4) 105.1(6), 104.1(6)
F-C-F	109.2(7), 107.4(6) 107.6(7), 111.2(6) 110.1(7), 108.8(7)	109.1(8), 113.2(9) 105.9(7), 105.3(12) 102.5(14), 113.0(12)	111.2(9), 109.9(8) 108.6(9), 110.5(15) 106.9(11), 108.8(15)
C-S...S-C	11.6(8)	15.6(8)	149.0(10)

Table 4 Li-O bond geometries in  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  (Å, °)

Li(1)-O(11)	2.080(9)	Li(1)-O(13)	2.051(9)
Li(1)-O(14)	1.951(9)	Li(1)-O(31)	2.054(9)
Li(1)-O(33)	1.997(11)		
Li(2)-O(12)	2.088(10)	Li(2)-O(21)	2.350(11)
Li(2)-O(22)	1.931(10)	Li(2)-O(23)	1.965(10)
Li(2)-O(32)	1.888(10)		
O(11)-Li(1)-O(13)	84.1(3)	O(12)-Li(2)-O(22)	95.2(4)
O(11)-Li(1)-O(14)	93.7(4)	O(12)-Li(2)-O(23)	91.3(4)
O(11)-Li(1)-O(33)	92.8(4)	O(12)-Li(2)-O(32)	99.2(5)
O(13)-Li(1)-O(31)	87.8(4)	O(21)-Li(2)-O(22)	92.6(4)
O(14)-Li(1)-O(31)	97.5(4)	O(21)-Li(2)-O(23)	79.6(4)
O(31)-Li(1)-O(33)	85.5(4)	O(21)-Li(2)-O(32)	83.8(4)
O(13)-Li(1)-O(14)	122.1(5)	O(22)-Li(2)-O(23)	115.1(5)
O(13)-Li(1)-O(33)	126.6(5)	O(22)-Li(2)-O(32)	112.2(5)
O(14)-Li(1)-O(33)	111.3(4)	O(23)-Li(2)-O(32)	130.2(5)
O(11)-Li(1)-O(31)	168.5(5)	O(12)-Li(2)-O(21)	169.9(5)

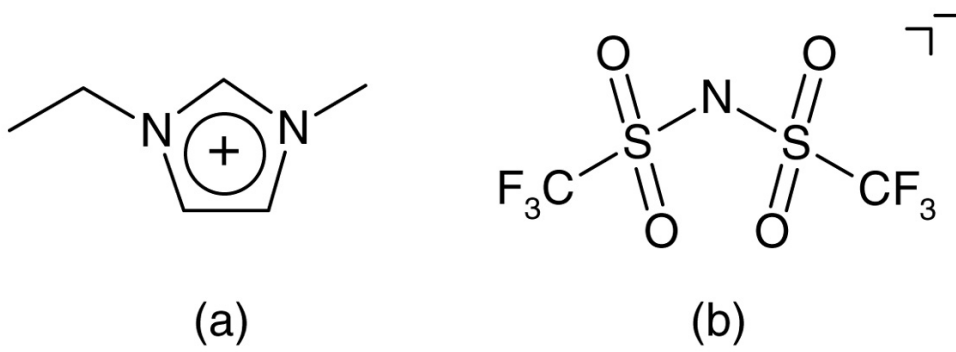


Fig. 1 Structures of (a) EMIm cation and (b)  $N(\text{SO}_2\text{CF}_3)_2$  anion.

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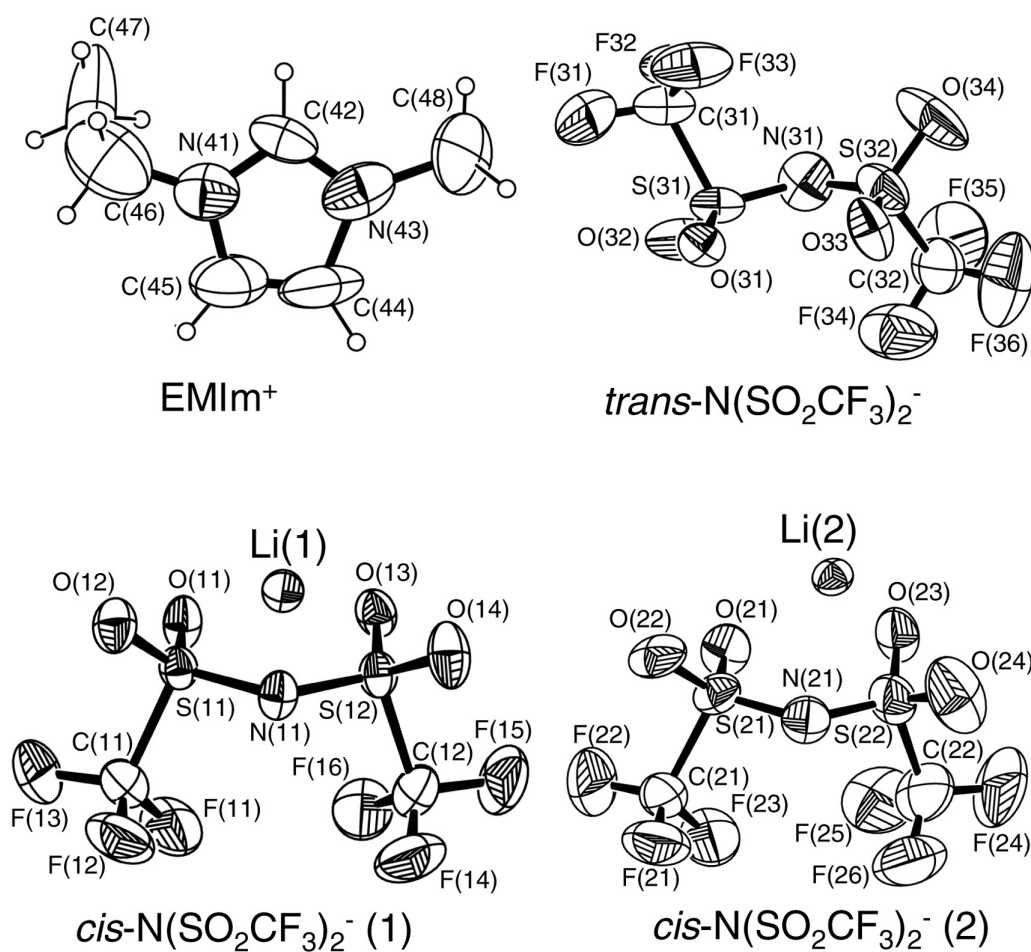


Fig. 2 Thermal ellipsoid plot of the individual ions in the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  asymmetric unit with atom numbering scheme. Li cations are drawn with the *cis*- conformation  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anions and H atoms are drawn as small circles of arbitrary radii.

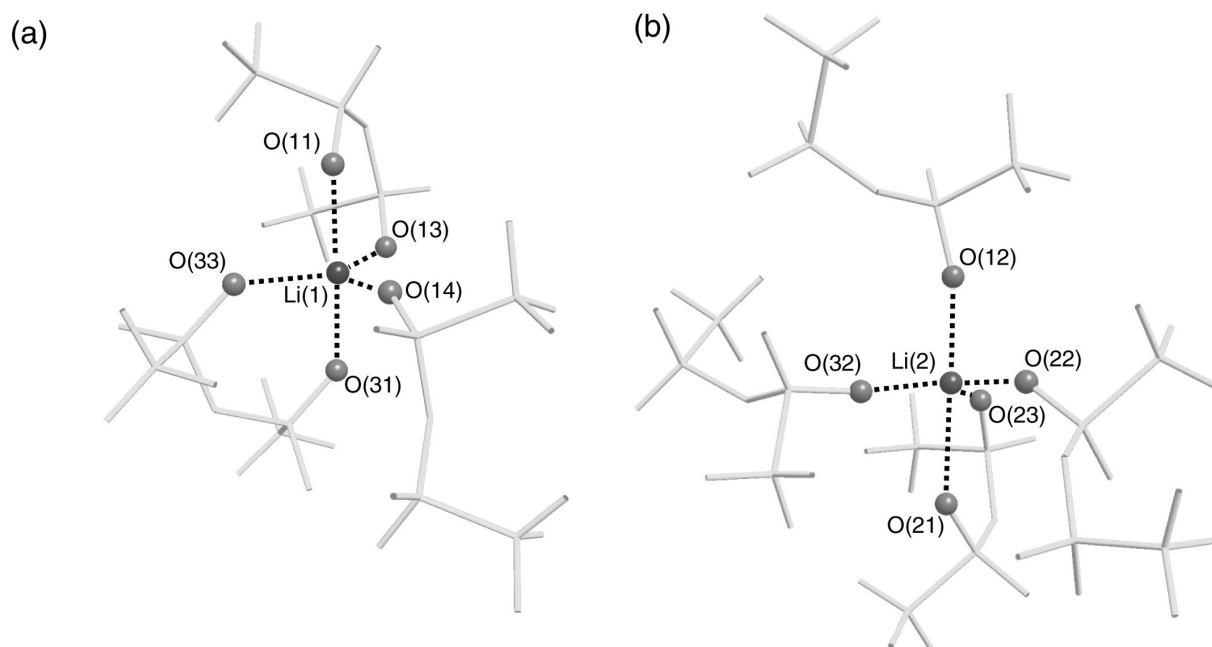


Fig. 3 Coordination environment around  $\text{Li}^+$  in the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  structure for (a)  $\text{Li}(1)$  and (b)  $\text{Li}(2)$ . The anion is drawn in a stick model except for oxygen atoms that link to  $\text{Li}^+$ .



*Fig. 4 Perspective view of the  $\text{Li}_2(\text{EMIm})(\text{N}(\text{SO}_2\text{CF}_3)_2)_3$  structure from the  $b$ -axis. Large circles denote fluorine atoms. Li-O bonds are drawn in solid lines and H atoms are omitted for clarity.*

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