

1-Methyl-1*H*-imidazol-3-ium methanesulfonate

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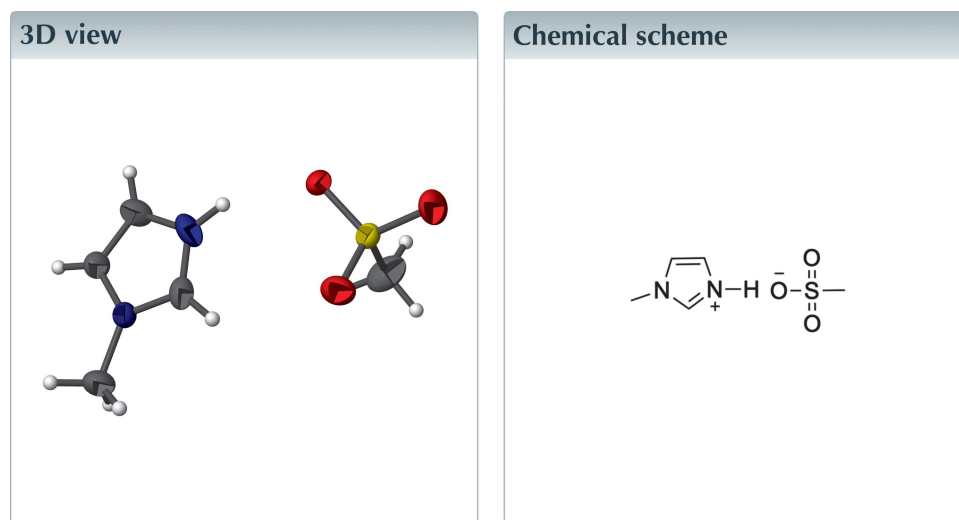
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Structural data: full structural data are available from iucrdata.iucr.org

The structure of the title salt, $C_4H_7N_2^+ \cdot CH_3O_3S^-$, has monoclinic ($P2_1/n$) symmetry. The 1-methylimidazolium cation and the methylsulfonate anion in the asymmetric unit are held together by a strong $N-H \cdots O$ hydrogen bond.



Structure description

Ionic liquids (ILs) with fluoride anions possess high electrochemical stability and electrical conductivity (Hmissa *et al.*, 2018). Fluoride ionic liquids were produced to serve as potential non-volatile replacements of VOCs for the development of IL electrolytes.

Electrolytes with stable solvents can be utilized for the production of innocuous rechargeable Al-ion and Li-ion batteries. The reported strategy for the synthesis of ILs with fluoride anions is autocatalytic, HF-free, and does not require chromatographic purification. HF-free synthesis of fluoride ionic liquids eradicates the need for corrosive acids. The exposure of the ionic liquid to water may serve as a technique to increase electrical conductivity (Li *et al.*, 2007). Chemical stability studies indicate that water attacks the S^{VI} atom, which leads to the formation of a sulfate-based salt (Fig. 1).

Sulfur(VI) fluoride-exchange (SuFEx) chemistry possesses characteristics of click chemistry. Many of its potential applications have been investigated recently, including post-polymerization modification (Yatvin *et al.*, 2015) and sulfonimidoyl fluorides synthesis (Gao *et al.*, 2018). Fluoride salts have been reported to function as catalysts for the SuFEx reaction (Gao *et al.*, 2017). The autocatalytic property of the sulfonyl-based ionic liquids allows the reaction to proceed in a time-efficient manner, opening the doors for potential industrial scale application. The chemical stability of these ionic liquids towards the hydrolysis reaction was studied in this work.

The title compound crystallizes in the monoclinic $P2_1/n$ space group. The 1-methylimidazolium cation and the methylsulfonate anion in the asymmetric unit are linked by a

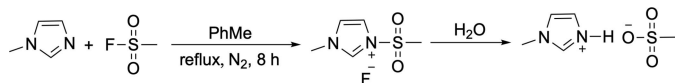


Figure 1
Synthetic scheme for the synthesis of imidazolium-based salts, paired with sulfate anion *via* SuFEx click chemistry

strong O \cdots H–N hydrogen bond [O \cdots N distance = 2.775 (2) Å; Table 1 and (Fig. 2)] between the proton on N and one of the sulfonate oxygen atoms. The packing is shown in Fig. 3.

1-MeIm is a common cation found in as many as 48 crystal structures in the Cambridge Structural Database (Groom *et al.*, 2016). The planar cation often displays π – π interactions with neighboring 1-MeIm cations (Wilkes & Zaworotko, 1993). Such interactions are not seen in the title compound. One of the methylsulfonate O atoms displays some degree of interaction with the π -cation [O–centroid distance = 3.382 (1) Å].

Synthesis and crystallization

One molar equivalent of 1-methylimidazole and methanesulfonyl fluoride were dissolved separately using 10 ml extra dry toluene. The two solutions were combined and stirred vigorously for 8 h at reflux temperature. Subsequent to reflux, 1 ml of deionized water was added to the reaction mixture dropwise and then stirred for 4 h at 60°C to allow for hydrolysis to occur. The solid phase of the reaction mixture was filtered. Colourless plate-like crystals formed after 29 days upon slow evaporation of the reaction solvent (toluene).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We are grateful to Professor Raphael G. Raptis (FIU) for the access to the X-ray diffractometer facility.

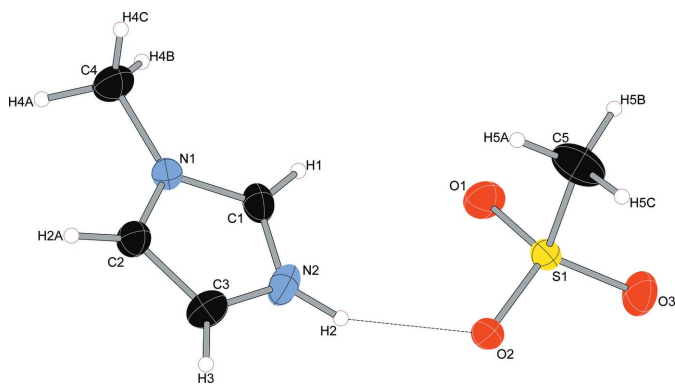


Figure 2
The asymmetric unit with displacement ellipsoids shown at the 35% probability level. The N–H \cdots O hydrogen bond (Table 1) is indicated by a dashed line.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
N2–H2 \cdots O2	0.87	1.96	2.775 (2)	156

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₄ H ₇ N ₂ ⁺ ·CH ₃ O ₃ S [−]
<i>M</i> _r	178.21
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	230
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.1891 (5), 7.4627 (4), 11.4884 (6)
β (°)	111.635 (1)
<i>V</i> (Å ³)	812.02 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.36
Crystal size (mm)	0.58 × 0.4 × 0.36
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T</i> _{min} , <i>T</i> _{max}	0.707, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	11035, 2011, 1827
<i>R</i> _{int}	0.015
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.668
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.085, 1.08
No. of reflections	2011
No. of parameters	102
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.23, −0.33

Computer programs: *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Funding information

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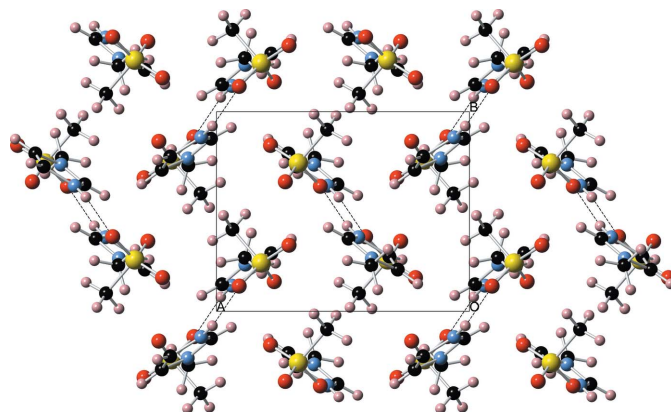


Figure 3
A view of the crystal packing of the title compound.

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full crystallographic data

IUCrData (2018). 3, x181781 [https://doi.org/10.1107/S2414314618017819]

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1-Methyl-1*H*-imidazol-3-ium methanesulfonate*Crystal data*

$C_4H_7N_2^+ \cdot CH_3O_3S^-$

$M_r = 178.21$

Monoclinic, $P2_1/n$

$a = 10.1891$ (5) Å

$b = 7.4627$ (4) Å

$c = 11.4884$ (6) Å

$\beta = 111.635$ (1)°

$V = 812.02$ (7) Å³

$Z = 4$

$F(000) = 376$

$D_x = 1.458$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9900 reflections

$\theta = 3.3$ – 28.3 °

$\mu = 0.36$ mm⁻¹

$T = 230$ K

Block, colourless

$0.58 \times 0.4 \times 0.36$ mm

Data collection

Bruker D8 Quest CMOS
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 10.42 pixels mm⁻¹

φ and ω shutterless scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.707$, $T_{\max} = 0.746$

11035 measured reflections

2011 independent reflections

1827 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 3.3$ °

$h = -13 \rightarrow 13$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.085$

$S = 1.08$

2011 reflections

102 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.3268P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.67678 (3)	0.74219 (4)	0.90924 (3)	0.02711 (11)
O1	0.72814 (12)	0.64890 (15)	0.82397 (10)	0.0424 (3)
O2	0.58946 (10)	0.62642 (13)	0.95480 (8)	0.0354 (2)
O3	0.78655 (11)	0.83115 (16)	1.01095 (10)	0.0468 (3)
N1	0.38601 (11)	0.26564 (14)	0.59635 (10)	0.0283 (2)
N2	0.43894 (12)	0.37124 (16)	0.78128 (11)	0.0384 (3)
H2	0.483452	0.427925	0.850900	0.046*
C1	0.47811 (14)	0.36423 (18)	0.68438 (13)	0.0349 (3)
H1	0.558245	0.420035	0.678699	0.042*
C2	0.28337 (14)	0.2092 (2)	0.63836 (13)	0.0347 (3)
H2A	0.204560	0.137987	0.594256	0.042*
C3	0.31699 (16)	0.2752 (2)	0.75517 (14)	0.0408 (3)
H3	0.266479	0.258443	0.808246	0.049*
C4	0.38835 (18)	0.2315 (2)	0.47203 (14)	0.0456 (4)
H4A	0.362591	0.107785	0.448925	0.068*
H4B	0.482460	0.253917	0.472837	0.068*
H4C	0.321550	0.310260	0.411695	0.068*
C5	0.56302 (18)	0.9098 (3)	0.81923 (19)	0.0552 (4)
H5A	0.484569	0.854603	0.752852	0.083*
H5B	0.614304	0.987198	0.782942	0.083*
H5C	0.527445	0.980152	0.872276	0.083*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02786 (17)	0.02531 (17)	0.02782 (17)	−0.00194 (10)	0.00987 (13)	0.00137 (11)
O1	0.0502 (6)	0.0444 (6)	0.0383 (5)	0.0050 (5)	0.0228 (5)	−0.0008 (4)
O2	0.0419 (5)	0.0357 (5)	0.0285 (4)	−0.0136 (4)	0.0128 (4)	−0.0001 (4)
O3	0.0407 (6)	0.0527 (7)	0.0441 (6)	−0.0190 (5)	0.0121 (5)	−0.0124 (5)
N1	0.0306 (5)	0.0254 (5)	0.0270 (5)	−0.0018 (4)	0.0083 (4)	−0.0002 (4)
N2	0.0388 (6)	0.0354 (6)	0.0303 (5)	0.0046 (5)	0.0003 (5)	−0.0091 (5)
C1	0.0307 (6)	0.0276 (6)	0.0396 (7)	−0.0027 (5)	0.0051 (5)	−0.0006 (5)
C2	0.0318 (6)	0.0393 (7)	0.0323 (7)	−0.0074 (5)	0.0109 (5)	−0.0032 (6)
C3	0.0397 (7)	0.0510 (9)	0.0325 (7)	0.0027 (6)	0.0142 (6)	−0.0034 (6)
C4	0.0545 (9)	0.0541 (9)	0.0333 (7)	−0.0080 (7)	0.0220 (7)	−0.0044 (6)
C5	0.0492 (9)	0.0469 (9)	0.0735 (11)	0.0159 (7)	0.0271 (8)	0.0264 (9)

Geometric parameters (\AA , $^\circ$)

S1—O1	1.4478 (10)	C1—H1	0.9400
S1—O2	1.4680 (9)	C2—H2A	0.9400
S1—O3	1.4468 (10)	C2—C3	1.350 (2)
S1—C5	1.7590 (16)	C3—H3	0.9400
N1—C1	1.3210 (17)	C4—H4A	0.9700
N1—C2	1.3699 (17)	C4—H4B	0.9700

N1—C4	1.4596 (17)	C4—H4C	0.9700
N2—H2	0.8700	C5—H5A	0.9700
N2—C1	1.3149 (19)	C5—H5B	0.9700
N2—C3	1.369 (2)	C5—H5C	0.9700
O1—S1—O2	112.08 (6)	C3—C2—H2A	126.5
O1—S1—C5	105.57 (8)	N2—C3—H3	126.7
O2—S1—C5	105.88 (7)	C2—C3—N2	106.63 (13)
O3—S1—O1	113.73 (7)	C2—C3—H3	126.7
O3—S1—O2	111.83 (6)	N1—C4—H4A	109.5
O3—S1—C5	107.10 (9)	N1—C4—H4B	109.5
C1—N1—C2	108.71 (11)	N1—C4—H4C	109.5
C1—N1—C4	125.66 (12)	H4A—C4—H4B	109.5
C2—N1—C4	125.53 (12)	H4A—C4—H4C	109.5
C1—N2—H2	125.4	H4B—C4—H4C	109.5
C1—N2—C3	109.15 (12)	S1—C5—H5A	109.5
C3—N2—H2	125.4	S1—C5—H5B	109.5
N1—C1—H1	125.7	S1—C5—H5C	109.5
N2—C1—N1	108.58 (12)	H5A—C5—H5B	109.5
N2—C1—H1	125.7	H5A—C5—H5C	109.5
N1—C2—H2A	126.5	H5B—C5—H5C	109.5
C3—C2—N1	106.92 (12)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2...O2	0.87	1.96	2.775 (2)	156
