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Crystal structure of (2*R*)-1-[(methylsulfonyl)oxy]propan-2-aminium chloride: a chiral molecular salt

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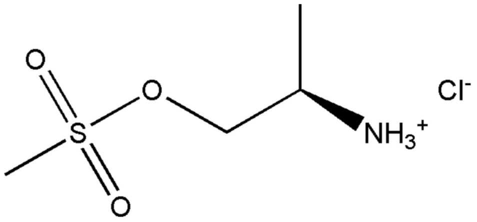
In the title chiral molecular salt, $C_4H_{12}NO_3S^+\cdot Cl^-$, the cation is protonated at the N atom, producing $[RNH_3]^+$, where *R* is $CH_3SO_2OCH_2C(H)CH_3$. The N atom in the cation is *sp*^{3}-hybridized. In the crystal, cations and anions are connected by strong N—H⋯Cl hydrogen bonds to generate edge-shared 12-membered rings of the form $\{\cdots Cl\cdots HNH\}_3$. This pattern of hydrogen bonding gives rise to zigzag supramolecular layers in the *ab* plane. The layers are connected into a three-dimensional architecture by C—H⋯O hydrogen bonds. The structure was refined as an inversion twin.

Keywords: crystal structure; chiral methanesulfonate; hydrogen bonding; salt.

CCDC reference: 1420721

1. Related literature

For background to chiral 2-amino-2-(alkyl/aryl/aralkyl)ethyl methanesulfonate hydrochlorides, see: Braghiroli & Di Bella (1996); Higashiura *et al.* (1989); Morgan *et al.* (1991); Pollack *et al.* (1989); Xu (2002).



2. Experimental

2.1. Crystal data

$C_4H_{12}ClNO_3S^+\cdot Cl^-$
M_r = 189.66
Monoclinic, $P2_1$
a = 5.4012 (1) Å
b = 8.2178 (2) Å
c = 10.2713 (2) Å
β = 94.534 (1)°
V = 454.48 (2) Å^3
Z = 2
Cu *Kα* radiation
μ = 5.57 mm^{-1}
T = 296 K
0.24 × 0.20 × 0.16 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.302, T_{max} = 0.410
2476 measured reflections
1387 independent reflections
1385 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.11
1387 reflections
96 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.08 (3)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1*E*⋯Cl1	0.89	2.33	3.169 (3)	156
C3—H3*A*⋯O3^{i}	0.97	2.58	3.428 (4)	147
N1—H1*D*⋯Cl1^{ii}	0.89	2.24	3.116 (3)	169
N1—H1*F*⋯Cl1^{iii}	0.89	2.26	3.139 (3)	171
C2—H2*A*⋯O2^{iv}	0.98	2.44	3.186 (4)	133
C4—H4*B*⋯O3^{v}	0.96	2.50	3.250 (4)	135
C4—H4*C*⋯O2^{vi}	0.96	2.51	3.438 (5)	163

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+2$; (ii) $-x+1, y-\frac{1}{2}, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, y-\frac{1}{2}, -z+2$; (v) $x+1, y, z$; (vi) $-x+1, y+\frac{1}{2}, -z+2$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5365).

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supporting information

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Crystal structure of (2*R*)-1-[(methylsulfonyl)oxy]propan-2-aminium chloride: a chiral molecular salt

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S1. Chemical context

The chiral 2-amino-2-(alkyl/aryl/aralkyl)ethyl methanesulfonate hydrochlorides are useful starting materials for the preparation of amines, benzoates, thiobenzoates, sulfonic acids, etc., as methanesulfonate is a very good leaving group in nucleophilic substitution reactions. The chiral 2-(alkyl/aryl/aralkyl)ethanesulfonic acid derivatives and sulfonopeptides (Higashiura *et al.*, 1989) occur in high concentrations in many mammalian tissues. These compounds are involved in various important physiological processes and are used as enzyme inhibitors and heptans in the development of catalytic anti-bodies (Braghiroli & Di Bella, 1996). The enantiomers of chiral 2-(alkyl/aryl/aralkyl)ethanesulfonic acid derivatives mimic the hypotensive effect of taurine (2-aminoethanesulfonic acid), one of the most abundant amino acids in mammals that seems to exhibit a special affinity for excitable tissues, such as brain, nerve and muscle (Xu *et al.*, 2002; Pollack *et al.*, 1989; Morgan *et al.*, 1991). In particular, the title compound was used in the synthesis of chiral amines by our group and as a part of our on-going research the structure of the title compound was determined.

S2. Structural commentary

In the title chiral molecular salt, $C_4H_{12}NO_3S^+.Cl^-$, the N atom is protonated resulting the cation $[RNH_3]^+$ where R is $CH_3SO_2OCH_2CH(CH_3)$- and the anion is chloride ion $[Cl]^-$. The N atom in the cation is sp^3 hybridized and the bond angles represents that the cation has tetrahedral structure around N (Fig. 1). In the crystal packing N—H···Cl hydrogen bonds connect ions into a supramolecular assembly in the *ab* plane (Fig. 2 and Table 1). Further, there exist C—H···O hydrogen bonds that connect the layers into a three-dimensional architecture.

S3. Synthesis and crystallization

The title chiral molecular salt was synthesised as per the literature procedure (Higashiura *et al.*, 1989). An aqueous solution of HCl (4 M, 12 ml) was added to a stirred solution of (2*R*)-2-[(*tert*-butoxycarbonyl)amino] propyl methanesulfonate (2.53 g, 10 mmol) in dioxane (15 ml). The resulting mixture was stirred for a further 1 h. The solution was then concentrated under reduced pressure and the residue obtained was recrystallized from hot ethanol to afford colourless single crystals suitable for single crystal X-ray diffraction.

S4. Refinement details

The H atom of the NH_3 group was located in a difference map but refined with N—H = 0.89, and with U_{iso}(H) = 1.2U_{eq}(N). Similarly, the other H atoms were positioned with idealized geometry using a riding model with C—H = 0.96–0.98 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(C). The structure was refined as an inversion twin with a Flack parameter of 0.08 (3)

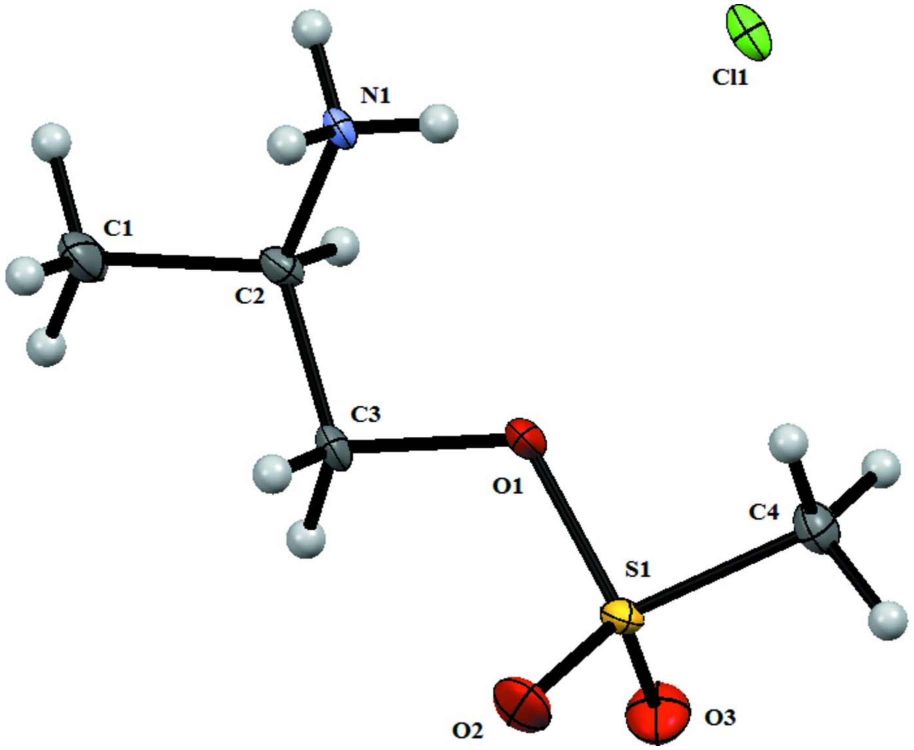

Figure 1

Molecular structure of the title molecular salt showing displacement ellipsoids drawn at the 50% probability level.

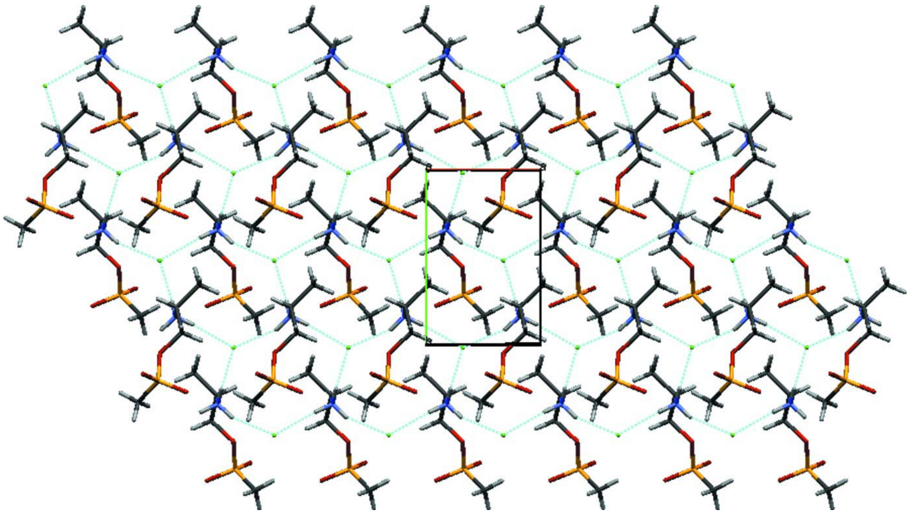

Figure 2

The molecular packing of the title molecular salt with N—H···Cl hydrogen bonds (aqua bonds) leading to a supramolecular assembly in the *ab* plane.

(2*R*)-2-Azaniumylpropyl methanesulfonate chloride

Crystal data

$C_4H_{12}ClNO_3S^{+}\cdot Cl^{-}$
$M_r = 189.66$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 5.4012$ (1) Å
$b = 8.2178$ (2) Å
$c = 10.2713$ (2) Å
$\beta = 94.534$ (1)°
$V = 454.48$ (2) Å^3
$Z = 2$
$F(000) = 200$

prism
$D_x = 1.386$ Mg m^{-3}
Melting point: 354 K
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 830 reflections
$\theta = 4.3$–64.7°
$\mu = 5.57$ mm^{-1}
$T = 296$ K
Prism, colourless
0.24 × 0.20 × 0.16 mm

Data collection

Bruker APEXII CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 2.01 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2013)
$T_{\min} = 0.302$, $T_{\max} = 0.410$

2476 measured reflections
1387 independent reflections
1385 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.029$
$\theta_{\max} = 64.7°$, $\theta_{\min} = 4.3°$
$h = -6 \rightarrow 2$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.11$
1387 reflections
96 parameters
1 restraint
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.0553P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2014), $Fc^{*}=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.120 (8)
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.08 (3)

Special details

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

Refinement. Refined as a 2-component inversion twin.

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

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
C1	−0.0227 (7)	0.1587 (5)	0.7527 (4)	0.0204 (8)
H1A	−0.1807	0.2029	0.7211	0.031*
H1B	−0.0282	0.1268	0.8423	0.031*

H1C	0.0142	0.0655	0.7013	0.031*
Cl1	0.67754 (13)	0.51693 (10)	0.53323 (7)	0.0149 (3)
S1	0.33444 (13)	0.70873 (9)	0.88988 (7)	0.0118 (3)
O1	0.3212 (4)	0.5513 (3)	0.8028 (2)	0.0190 (6)
N1	0.1849 (5)	0.3392 (4)	0.6037 (3)	0.0111 (6)
H1D	0.2153	0.2535	0.5544	0.013*
H1E	0.3047	0.4127	0.5982	0.013*
H1F	0.0395	0.3828	0.5759	0.013*
C2	0.1771 (6)	0.2864 (4)	0.7423 (3)	0.0119 (7)
H2A	0.3383	0.2394	0.7725	0.014*
O3	0.0905 (4)	0.7735 (4)	0.8958 (3)	0.0225 (6)
C3	0.1271 (6)	0.4323 (5)	0.8265 (3)	0.0140 (7)
H3B	−0.0362	0.4770	0.8021	0.017*
H3A	0.1358	0.4019	0.9180	0.017*
C4	0.5119 (6)	0.8308 (5)	0.7941 (3)	0.0159 (7)
H4B	0.6647	0.7763	0.7801	0.024*
H4C	0.5475	0.9323	0.8380	0.024*
H4A	0.4212	0.8512	0.7116	0.024*
O2	0.4703 (5)	0.6718 (4)	1.0115 (2)	0.0241 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0242 (19)	0.0177 (18)	0.0211 (17)	−0.0055 (15)	0.0130 (14)	−0.0007 (15)
Cl1	0.0110 (4)	0.0182 (5)	0.0161 (4)	−0.0006 (3)	0.0051 (3)	0.0047 (3)
S1	0.0117 (4)	0.0156 (5)	0.0085 (4)	−0.0016 (3)	0.0030 (3)	−0.0020 (3)
O1	0.0205 (13)	0.0198 (14)	0.0186 (12)	−0.0093 (10)	0.0134 (9)	−0.0075 (11)
N1	0.0094 (13)	0.0128 (15)	0.0118 (13)	−0.0016 (11)	0.0051 (10)	−0.0004 (11)
C2	0.0117 (15)	0.0138 (17)	0.0110 (15)	0.0003 (13)	0.0052 (12)	0.0003 (13)
O3	0.0138 (12)	0.0264 (14)	0.0283 (14)	0.0026 (11)	0.0088 (10)	−0.0058 (11)
C3	0.0120 (15)	0.0159 (17)	0.0152 (17)	−0.0047 (15)	0.0076 (12)	−0.0014 (16)
C4	0.0158 (16)	0.0165 (17)	0.0158 (16)	−0.0032 (15)	0.0044 (12)	0.0020 (15)
O2	0.0278 (14)	0.0330 (17)	0.0107 (12)	−0.0060 (12)	−0.0040 (9)	0.0035 (11)

Geometric parameters (Å, º)

C1—C2	1.515 (5)	N1—H1D	0.8900
C1—H1A	0.9600	N1—H1E	0.8900
C1—H1B	0.9600	N1—H1F	0.8900
C1—H1C	0.9600	C2—C3	1.515 (5)
S1—O3	1.427 (3)	C2—H2A	0.9800
S1—O2	1.430 (3)	C3—H3B	0.9700
S1—O1	1.571 (3)	C3—H3A	0.9700
S1—C4	1.744 (4)	C4—H4B	0.9600
O1—C3	1.468 (4)	C4—H4C	0.9600
N1—C2	1.491 (4)	C4—H4A	0.9600
C2—C1—H1A	109.5	N1—C2—C1	110.1 (3)

C2—C1—H1B	109.5	N1—C2—C3	109.5 (3)
H1A—C1—H1B	109.5	C1—C2—C3	110.3 (3)
C2—C1—H1C	109.5	N1—C2—H2A	109.0
H1A—C1—H1C	109.5	C1—C2—H2A	109.0
H1B—C1—H1C	109.5	C3—C2—H2A	109.0
O3—S1—O2	116.97 (15)	O1—C3—C2	105.7 (2)
O3—S1—O1	109.32 (15)	O1—C3—H3B	110.6
O2—S1—O1	108.65 (17)	C2—C3—H3B	110.6
O3—S1—C4	111.10 (17)	O1—C3—H3A	110.6
O2—S1—C4	110.34 (16)	C2—C3—H3A	110.6
O1—S1—C4	98.91 (16)	H3B—C3—H3A	108.7
C3—O1—S1	117.07 (19)	S1—C4—H4B	109.5
C2—N1—H1D	109.5	S1—C4—H4C	109.5
C2—N1—H1E	109.5	H4B—C4—H4C	109.5
H1D—N1—H1E	109.5	S1—C4—H4A	109.5
C2—N1—H1F	109.5	H4B—C4—H4A	109.5
H1D—N1—H1F	109.5	H4C—C4—H4A	109.5
H1E—N1—H1F	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*E*···Cl1	0.89	2.33	3.169 (3)	156
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