

Rubidium bis(trifluoromethanesulfonyl)imidate dioxane disolvate

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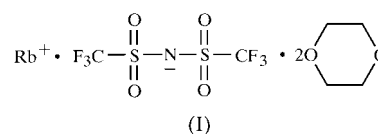
The bis(trifluoromethanesulfonyl)imidate anion crystallizes with Rb as the title dioxane 1:2 solvate, $\text{Rb}^+ \cdot \text{CF}_3\text{SO}_2\text{N}(\text{SO}_2\text{CF}_3)^- \cdot 2\text{C}_4\text{H}_8\text{O}_2$, with the anion in a *transoid* conformation, as opposed to the *cisoid* form typically seen when there are significant cation–anion interactions. The Rb^+ cation is eight-coordinate, interacting with one anion in a chelating fashion and with two other anions through the remaining sulfonyl O atoms. The latter interactions link ion pairs through the formation of Rb_2O_2 dimers about inversion centers at $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, forming extended columns which run parallel to the *a* axis of the unit cell. Rb–dioxane bridges crosslink these salt columns in the (010), (001) and (011) directions, resulting in a three-dimensional network solid. One dioxane solvent molecule is disordered over two half-occupancy sites.

Comment

Salts of bis(perfluoroalkanesulfonyl)imides, particularly the trifluoromethyl derivatives, have been found to serve as solutes for polymer electrolytes, leading to dramatically improved performance (Armand *et al.*, 1990; Nowinski *et al.*, 1994). This behavior is due in part to the remarkable acidity of these compounds (Koppel *et al.*, 1994; DesMarteau, 1995). The resonance stabilization of the conjugate base anions of the acids results from extensive delocalization of charge over the $\text{SO}_2\text{—N—SO}_2$ framework. With cations offering no strong interactions, these anions have been found to give salts with good potential as ionic liquids (Golding *et al.*, 1998). On the other hand, with metal cations they serve as multidentate ligands that bond to multiple metal centers to maximize electrostatic interaction (DesMarteau *et al.*, 1989, 1992; Xue *et al.*, 1997, 2002). These interactions result in the formation of ionic hydrophilic and perfluoroalkyl hydrophobic regions, which typically associate into layers consisting of an ionic core with perfluoroalkyl surfaces. This fluorine segregation effect (Dautel *et al.*, 2002; Wolff *et al.*, 1999) may provide a feasible

driving force for the directed design of new solid-state materials.

As we (Xue *et al.*, 1997, 2002) and others (Zak & Ruzicka, 1998) have observed, bis(perfluoroalkanesulfonyl)imides can exist in two different conformations as the anion, either in a *transoid* form, with the perfluoroalkyl groups lying on opposite sides of the S–N–S plane ($\text{C—S} \cdots \text{S—C}$ dihedral angle of $\sim 180^\circ$), or in a *cisoid* form, with the perfluoroalkyl groups lying on the same side of the S–N–S plane ($\text{C—S} \cdots \text{S—C}$ dihedral angle of $\sim 0^\circ$). It has been our general experience that the *transoid* form is favored when there are only weak cation–anion interactions, but that the *cisoid* form is often found when the anion is chelated to a metal center. In a recent contribution (Xue *et al.*, 2002), the anion was found in the *cisoid* form in anhydrous and hydrated salts of all the alkali metal cations except rubidium, which was determined as the monohydrate salt. We report here the structure of the title dioxane solvate, (I), of the rubidium salt and, like the monohydrate form, the anion has a *transoid* conformation [$\text{C—S} \cdots \text{S—C}$ dihedral angle of $-147.2(4)^\circ$].



The distances and angles within the anion of (I) agree well with those of other salts (DesMarteau *et al.*, 1989, 1992; Xue *et al.*, 1997, 2002; Haas *et al.*, 1996; Mikami *et al.*, 1998; Polyakov

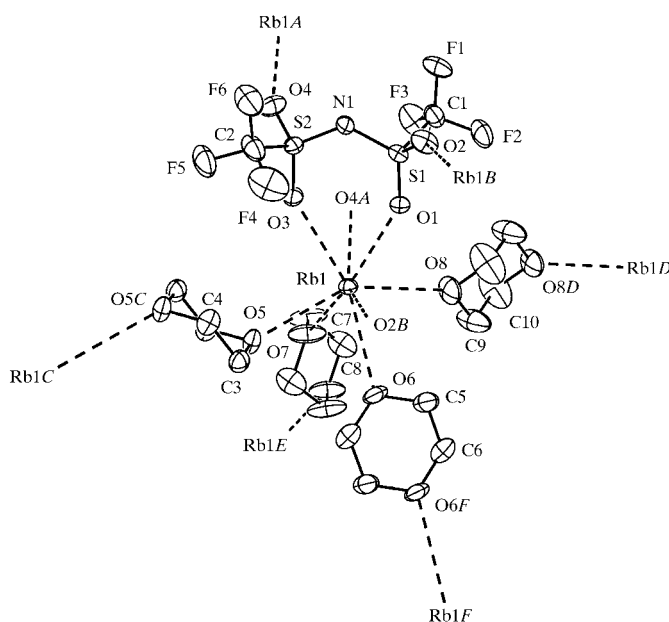


Figure 1
The molecular structure of (I) and four bridging dioxane molecules. Only one component of the disordered dioxane molecule (atoms O8, C9 and C10) is shown and H atoms have been omitted. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (A) $-x, 1-y, -z$; (B) $1-x, 1-y, -z$; (C) $1-x, 2-y, -z$; (D) $1-x, 1-y, 1-z$; (E) $1-x, 2-y, 1-z$; (F) $2-x, 2-y, 1-z$.]

et al., 1999). The cation is eight-coordinate, with $\text{Rb}^+ \cdots \text{O}$ contacts ranging from 2.897 (4) to 3.063 (4) Å. These contacts are also within previously reported ranges for rubidium salts of this (Xue *et al.*, 2002; Zak & Ruzicka, 1998) and similar anions (Juschke *et al.*, 1997) and for rubidium dioxane solvates (Bryan *et al.*, 1998, 1999; Neander *et al.*, 2000; Edelmann *et al.*, 1992).

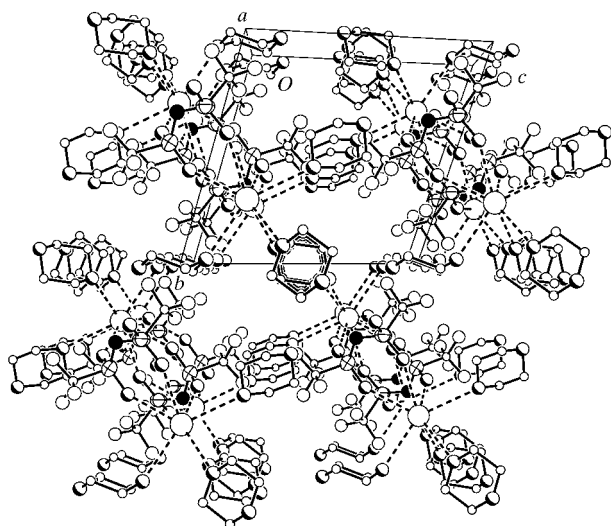


Figure 2

A packing diagram for (I), viewed down the a axis. S atoms are shown as 50% probability displacement ellipsoids, Rb^+ ions as large open circles, N atoms as solid circles, O atoms as partially shaded circles and C atoms as small open circles. H atoms are not shown.

The cation and anion of (I) sit upon general positions within the cell. The anion interacts with the cation through atoms O1 and O3 to form a chelate. Additional contacts through atom O2 about an inversion center at $(0, \frac{1}{2}, 0)$ and through atom O4 about $(\frac{1}{2}, \frac{1}{2}, 0)$ link ion pairs into columns running up the a axis. Each of the dioxane molecules is situated about an inversion center and bridges salt columns in the (010), (001) and (011) directions, to form a three-dimensional network solid.

Reasons for the observed preference of the *transoid* conformation of the anion with Rb are not yet clear, but investigation into this interesting behavior will continue.

Experimental

The title compound was synthesized by neutralization of a methanol solution of bis(trifluoromethanesulfonyl)imide in acid form with rubidium carbonate, followed by recrystallization from dioxane.

Crystal data

$\text{Rb}^+ \cdot \text{C}_2\text{F}_6\text{NO}_4\text{S}_2^- \cdot 2\text{C}_4\text{H}_8\text{O}_2$
 $M_r = 541.83$
 Triclinic, $P1$
 $a = 9.732$ (4) Å
 $b = 11.310$ (4) Å
 $c = 11.638$ (4) Å
 $\alpha = 94.61$ (3)°
 $\beta = 113.08$ (3)°
 $\gamma = 115.24$ (3)°
 $V = 1017.7$ (8) Å³

$Z = 2$
 $D_x = 1.768$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 50 reflections
 $\theta = 11.7$ – 17.8 °
 $\mu = 2.73$ mm⁻¹
 $T = 295$ (2) K
 Parallelepiped, colorless
 $0.41 \times 0.37 \times 0.26$ mm

Data collection

Nicolet *R3mV* diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 via ψ scan (*P3 Software*; Siemens, 1989)
 $T_{\min} = 0.342$, $T_{\max} = 0.492$
 3805 measured reflections
 3576 independent reflections
 2092 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 25.1$ °
 $h = -11 \rightarrow 0$
 $k = -12 \rightarrow 13$
 $l = -12 \rightarrow 13$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.037$
 $wR(F^2) = 0.061$
 $S = 1.00$
 3576 reflections
 272 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0032P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0148 (4)

Table 1

Selected geometric parameters (Å, °).

S1—O1	1.416 (3)	S2—O4	1.417 (4)
S1—O2	1.433 (3)	S2—O3	1.424 (3)
S1—N1	1.550 (4)	S2—N1	1.563 (4)
S1—C1	1.814 (6)	S2—C2	1.803 (7)
O1—S1—O2	118.8 (2)	O4—S2—C2	105.4 (4)
O1—S1—C1	104.8 (3)	O3—S2—C2	104.0 (3)
O2—S1—C1	102.9 (3)	N1—S2—C2	98.3 (3)
N1—S1—C1	100.0 (3)	S1—N1—S2	128.6 (3)
O4—S2—O3	119.4 (2)		

One of the dioxane molecules (atoms O8, C9 and C10) is disordered, with equally occupied alternative sites, C9' and C10', for the C atoms. Restraints were applied to the O—C and C—C distances, and the cross-ring C \cdots C, O \cdots C and O \cdots O contacts, and all the half-occupancy non-H atoms were refined with anisotropic displacement parameters. All H atoms were included in the structure-factor calculations using a riding model at optimized positions, with a C—H distance of 0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *P3 Software* (Siemens, 1989); cell refinement: *P3 Software*; data reduction: *SHELXTL* (Sheldrick, 2000); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1471). Services for accessing these data are described at the back of the journal.

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