Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Twinned $\alpha$-LiRb$_2$(CF$_3$SO$_3$)$_3$

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Received 3 July 2003
Accepted 30 September 2003
Online 8 November 2003

The investigated crystal of $\alpha$-LiRb$_2$(CF$_3$SO$_3$)$_3$ [lithium dirubidium tris(trifluoromethanesulfonate)] was a twin, with the twin matrix given by ($\bar{1}$00/010/001). The structure consists of channel-like patterns built up of lipophilic CF$_3$ groups pointing towards each other. The polar interstices are occupied by cations. One Rb atom is coordinated by O atoms in the form of a distorted square antiprism, while the coordination around the second Rb atom is best described as a distorted pentagonal plane, with one O atom and one F atom situated above and an additional F atom below this plane. The O atoms around the Li atom form a strongly distorted tetrahedron.

## Comment

Salts consisting of complex anions often show phase transitions to rotationally disordered modifications. As a rule, these phase transitions are accompanied by an increase in the ionic conductivity (Jansen, 1991). Alkali metal salts of the trifluoromethanesulfonate (triflate) ion belong to these so-called rotator phases. Due to their interesting properties, the ionic conductivities and crystal structures of, for example, $\beta$-LiSO$_3$CF$_3$ (Tremayne *et al.*, 1992; Bolte & Lerner, 2001), $\alpha$-NaSO$_3$CF$_3$ (Sofina *et al.*, 2003) and RT-KSO$_3$CF$_3$ (Korus & Jansen, 2001) have been studied in detail. Furthermore, mixed alkali triflates offer the possibility of exploring the 'mixed cation effect', which can be observed in ion-conducting systems containing more than one mobile cation (Yanija & Secco, 1995). The ionic conductivity of compounds in such systems can generally be varied by adjusting the ratio of the cations.

Against this background, we have carried out systematic investigations of the phase diagram of the LiSO$_3$CF$_3$/RbSO$_3$CF$_3$ system. In the course of these investigations, crystals of $\alpha$-LiRb$_2$(SO$_3$CF$_3$)$_3$ were found and the structure is presented here. The structure determination was rendered complicated due to underlying twinning.

In the structure of $\alpha$-LiRb$_2$(SO$_3$CF$_3$)$_3$, three crystallographically independent triflate ions can be distinguished. Their conformation is staggered and the observed bond lengths and angles are comparable with those in $\beta$-LiSO$_3$CF$_3$ (Bolte & Lerner, 2001), $\alpha$-NaSO$_3$CF$_3$(Sofina *et al.*, 2003), the low- and room-temperature modifications of NaSO$_3$CF$_3$·H$_2$O (Korus & Jansen, 1997), NaSO$_3$CF$_3$·3HSO$_3$CF$_3$ (Korus & Jansen, 1998) and RT-KSO$_3$CF$_3$ (Korus & Jansen, 2001).

In $\alpha$-LiRb$_2$(SO$_3$CF$_3$)$_3$, atom Rb1 is coordinated by O atoms in the form of a distorted square antiprism (Fig. 1). The cation is displaced towards the plane formed by atoms O1, O4, O7$^{\rm iv}$ and O9$^{\rm ii}$ [symmetry codes: (ii) $1 + x, y, z$; (iv) $-x, 2 - y, -z$]. Atom O5$^{\rm iii}$ is shifted from the ideal position and approaches atom O6$^{\rm iii}$, as both atoms are bridged by an S atom [symmetry code: (iii) $x - 1, y$, z]. Each of the remaining O atoms forms part of a different triflate ion.

Atom Rb2 is coordinated by five O atoms to form a distorted pentagonal plane (Fig. 1). The O2$^{\rm vi}$—Rb2—O4$^{\rm iv}$ angle is widened, as atoms O2$^{\rm vi}$ and O4$^{\rm iv}$ are again bridged by an S atom [symmetry code: (vi) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$]. The nearest atoms above the pentagonal plane are O7 and F1$^{\rm ii}$; that below the plane is atom F7, with a large distance to the central atom (4.20 Å).

The Li atom is surrounded by O atoms in the form of a strongly distorted tetrahedron, with an average Li—O distance of 1.95 Å (Fig. 1). This value is only slightly different from that observed in $\beta$-LiSO$_3$CF$_3$ (1.94 Å; Bolte & Lerner, 2001).

In the structures of the pure alkali triflates *M*SO$_3$CF$_3$ (*M* is Li or Na) which have been characterized to date (Bolte &

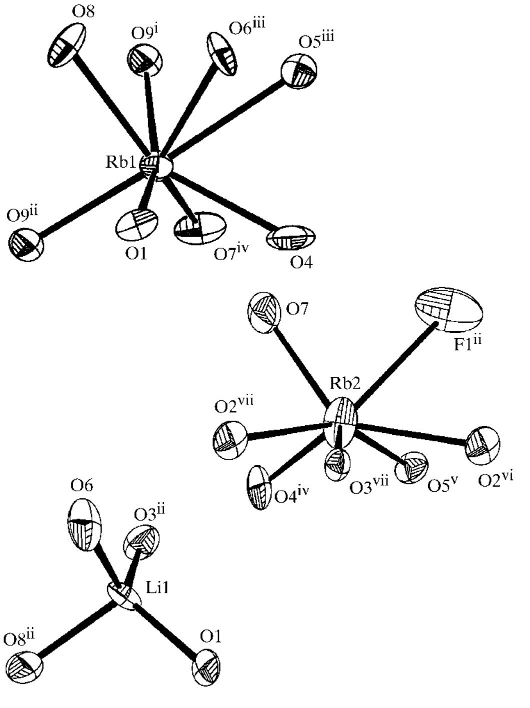

**Figure 1**
View of the coordination around the cations in $\alpha$-LiRb$_2$(SO$_3$CF$_3$)$_3$. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (i) $-1 - x, 2 - y, -z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $-x, 2 - y, -z$; (v) $1 - x, 2 - y, -z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (vii) $-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$].

DOI: 10.1107/S0108270103021693

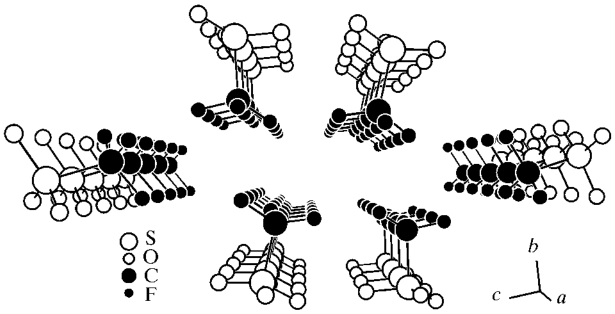

**Figure 2**
A perspective view of the channel-like pattern formed by the $CF_3$ groups in $\alpha$-$LiRb_2(SO_3CF_3)_3$.

Lerner, 2001; Sofina *et al.*, 2003), as well as in the structure of $NaSO_3CF_3{\cdot}H_2O$ (Korus & Jansen, 1997), the non-polar $CF_3$ groups point towards each other and form double layers which are linked by cations. In $\alpha$-$LiRb_2(SO_3CF_3)_3$ and RT-$KSO_3CF_3$ (Korus & Jansen, 2001), on the other hand, the $CF_3$ groups build up channel-like patterns along the crystallographic *a* axis (Fig. 2) and the polar interstices between these channels are filled with cations (Fig. 3).

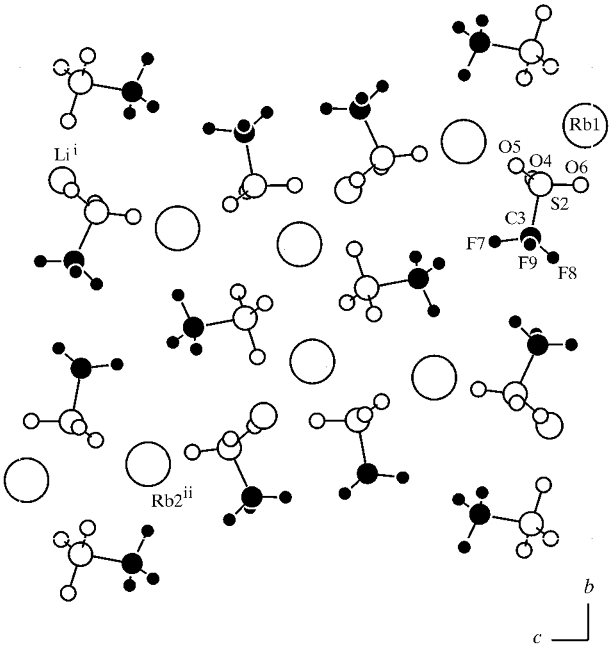

**Figure 3**
A projection on the *bc* plane of the structure of $\alpha$-$LiRb_2(SO_3CF_3)_3$. [Symmetry codes: (i) $x, y, z + 1$; (ii) $x + 1, y - 1, z + 1$.]

## Experimental

$\alpha$-$LiRb_2(CF_3SO_3)_3$ was prepared from mixtures of solid $LiSO_3CF_3$ (Aldrich, 99.995%) and $RbSO_3CF_3$. Details of the syntheses of both $\alpha$-$LiRb_2(SO_3CF_3)_3$ and $RbSO_3CF_3$ are described in Pompetzki *et al.* (2003). The 'single crystal' investigated in the present work was found within a diphasic product consisting of $LiRb_2(SO_3CF_3)_3$ and $Li_{0.55}Rb_{0.45}SO_3CF_3$, which had formed on annealing (533 K, 7 d, cooling rate of 5 K $h^{-1}$) a mixture of $LiSO_3CF_3$ (40 mol%) and $RbSO_3CF_3$ (60 mol%). The crystal was selected in a glove-box under dry argon.

*Crystal data*

$LiRb_2(CF_3SO_3)_3$
$M_r = 625.12$
Monoclinic, $P2_1/n$
$a = 5.3408\ (9)$ Å
$b = 16.286\ (2)$ Å
$c = 19.721\ (3)$ Å
$\beta = 90.480\ (10)^\circ$
$V = 1715.3\ (4)$ Å$^3$
$Z = 4$

$D_x = 2.42$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3752 reflections
$\theta = 4.8$–$59.1^\circ$
$\mu = 6.20$ mm$^{-1}$
$T = 293\ (2)$ K
Irregular, colourless
$0.15 \times 0.12 \times 0.08$ mm

*Data collection*

Bruker SMART-APEX CCD area-detector diffractometer
$\omega$ scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
$T_{min} = 0.062$, $T_{max} = 0.155$
21 958 measured reflections

5010 independent reflections
2625 reflections with $I > 3\sigma(I)$
$R_{int} = 0.114$
$\theta_{max} = 30.1^\circ$
$h = -7 \rightarrow 7$
$k = -22 \rightarrow 22$
$l = -27 \rightarrow 27$

*Refinement*

Refinement on $F^2$
$R(F) = 0.068$
$wR(F^2) = 0.061$
$S = 4.17$
5010 reflections

245 parameters
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.86$ e Å$^{-3}$
$\Delta\rho_{min} = -2.05$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Rb1—O4 | 2.904 (12) | Rb2—O2$^{vi}$ | 3.011 (11) |
| Rb1—O9$^{i}$ | 2.944 (11) | Rb2—O3$^{vii}$ | 3.100 (11) |
| Rb1—O9$^{ii}$ | 2.998 (11) | Rb2—O2$^{vii}$ | 3.188 (11) |
| Rb1—O6$^{iii}$ | 3.004 (10) | Rb2—O7 | 3.193 (13) |
| Rb1—O7$^{iv}$ | 3.014 (12) | Rb2—F1$^{ii}$ | 3.221 (12) |
| Rb1—O8 | 3.043 (10) | Li1—O3$^{ii}$ | 1.89 (3) |
| Rb1—O1 | 3.108 (10) | Li1—O6 | 1.91 (2) |
| Rb1—O5$^{iii}$ | 3.228 (11) | Li1—O1 | 1.94 (3) |
| Rb2—O5$^{v}$ | 2.870 (11) | Li1—O8$^{ii}$ | 2.06 (2) |
| Rb2—O4$^{iv}$ | 2.883 (13) | | |
| | | | |
| O3$^{ii}$—Li1—O6 | 113.2 (13) | O3$^{ii}$—Li1—O8$^{ii}$ | 105.8 (12) |
| O3$^{ii}$—Li1—O1 | 119.7 (12) | O6—Li1—O8$^{ii}$ | 99.0 (10) |
| O6—Li1—O1 | 110.6 (12) | O1—Li1—O8$^{ii}$ | 106.1 (11) |

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

The structure was solved in space group $P2_1/n$ *via* direct methods and the solution yielded the positions of the heavy atoms. The positions of the light atoms were found using a difference Fourier synthesis. Refinement as a single crystal stuck at an overall agreement factor of about 23%, and no satisfactory structural model could be obtained. Of course, the pseudo-orthorhombic metrics implied the possibility of twinning. Furthermore, the fact that differential scanning calorimetry measurements and X-ray powder diffraction studies confirmed a phase transition at approximately 383 K to a $\beta$ phase with orthorhombic metrics [$a = 5.476\ (2)$, $b = 16.554\ (18)$ and $c = 20.177\ (11)$ Å] suggested the introduction of an additional mirror plane from the orthorhombic system as a twinning operation. Consequently, we chose a mirror plane perpendicular to the *a* axis and introduced the corresponding twin matrix. The refinement converged satisfactorily after taking the twinning into account. The twin matrix was given by ($\bar{1}$00/010/001). The volume fractions of the twin individuals are $t_I = 0.515\ (2)$ and $t_{II} = 0.485\ (2)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *JANA*2000 (Petříček & Dušek, 2000); molecular graphics: *DIAMOND* (Bergerhoff *et al.*, 1996) and *ORTEP*-3 *for Windows* (Farrugia, 1996).

The authors gratefully acknowledge financial support by the BMBF (project No. 05KS1ESA/2).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1657). Services for accessing these data are described at the back of the journal.

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