

## Li<sup>+</sup> cation coordination in [Li<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(diglyme)] and [Li<sub>3</sub>(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub>(diglyme)]

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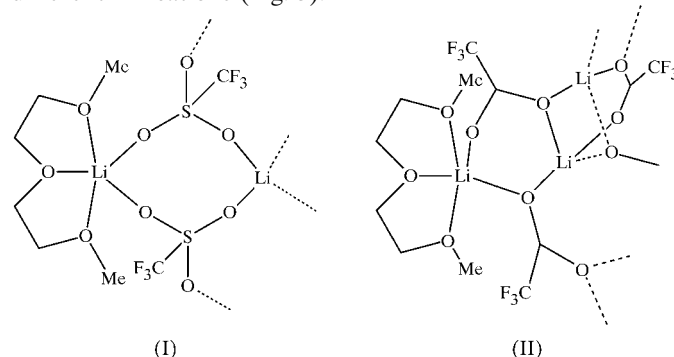
The title compounds, poly[[[bis(2-methoxyethyl) ether]-lithium(I)]-di- $\mu_3$ -trifluoromethanesulfonato-lithium(I)], [Li<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>n</sub>], and poly[[[bis(2-methoxyethyl) ether]-lithium(I)]-di- $\mu_3$ -trifluoroacetato-dilithium(I)- $\mu_3$ -trifluoroacetato], [Li<sub>3</sub>(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>n</sub>], consist of one-dimensional polymer chains. Both structures contain five-coordinate Li<sup>+</sup> cations coordinated by a tridentate diglyme [bis(2-methoxyethyl) ether] molecule and two O atoms, each from separate anions. In both structures, the [Li(diglyme)X<sub>2</sub>]<sup>-</sup> (X is CF<sub>3</sub>SO<sub>3</sub> or CF<sub>3</sub>CO<sub>2</sub>) fragments are further connected by other Li<sup>+</sup> cations and anions, creating one-dimensional chains. These connecting Li<sup>+</sup> cations are coordinated by four separate anions in both compounds. The CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anions, however, adopt different forms of cation coordination, resulting in differences in the connectivity of the structures and solvate stoichiometries.

### Comment

The structural characterizations of [Li<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>n</sub>], (I), and [Li<sub>3</sub>(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>n</sub>], (II), were performed as part of a comprehensive study of lithium-salt phase behavior with glyme ligands (Henderson, 2002). Single crystals of (I) and (II) were obtained during the preparation of samples for the determination of diglyme–LiCF<sub>3</sub>SO<sub>3</sub> and diglyme–LiCF<sub>3</sub>CO<sub>2</sub> phase diagrams. The exploration of such solvate structures provides insight into the properties of liquid electrolytes, as well as the poorly understood conductivity mechanisms in poly(ethylene oxide)–lithium salt solid electrolytes (Rhodes & Frech, 2001).

The structure of (I) contains two Li<sup>+</sup> cations, two CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions and one diglyme molecule in the asymmetric unit, all in general positions (Fig. 1). Atom Li1 is five-coordinate, coordinated by three ether O atoms from the diglyme and two O atoms from different CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions. Atom Li2 is four-

coordinate, with four different CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions coordinated to the cation through O atoms. Both of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions in the asymmetric unit are tridentate, coordinated to three different Li<sup>+</sup> cations (Fig. 3).



The structure of (II) contains three Li<sup>+</sup> cations, three CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anions and one diglyme molecule in the asymmetric unit, all in general positions (Fig. 2). Atom Li1 is five-coordinate, coordinated by three ether O atoms from the diglyme and two O atoms from different CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anions. Atoms Li2 and Li3 are four-coordinate, coordinated by four O atoms from different CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anions. The CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anions containing atoms C7 and C9 are both tridentate, with one O atom coordinated to two Li<sup>+</sup> cations and the other to only one cation. The CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> anion containing atom C11 has tetra-dentate coordination, with both O atoms coordinated to two Li<sup>+</sup> cations (Fig. 4).

One-dimensional polymeric chains are formed from the aggregation of the Li<sup>+</sup> cations and the anions in the two structures. The crystal structure of (I) contains an inversion center at the centroid of an –Li–O–S–O–Li–O–S–O– eight-atom ring. This connects two [Li(diglyme)] fragments together. The crystal structure of (II) contains two inversion centres, one at the centroid of an –Li–O–C–O–Li–O–C–O– eight-atom ring and one at the centroid of an –Li–O–Li–O– four-atom ring. The former connects two [Li(diglyme)] fragments together, while the latter also connects the [Li(diglyme)] fragments, but has other cations and anions linking the four-atom ring to the fragments, as outlined above.

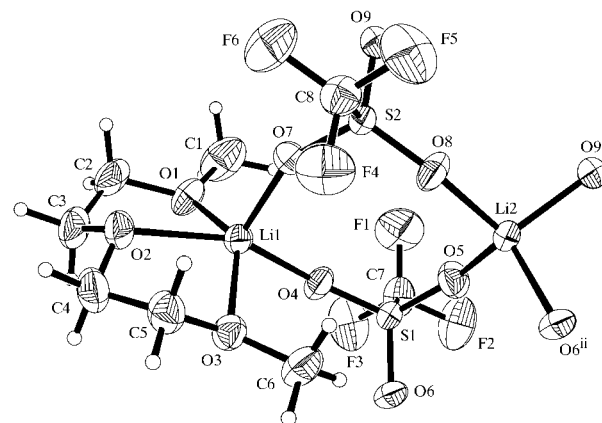
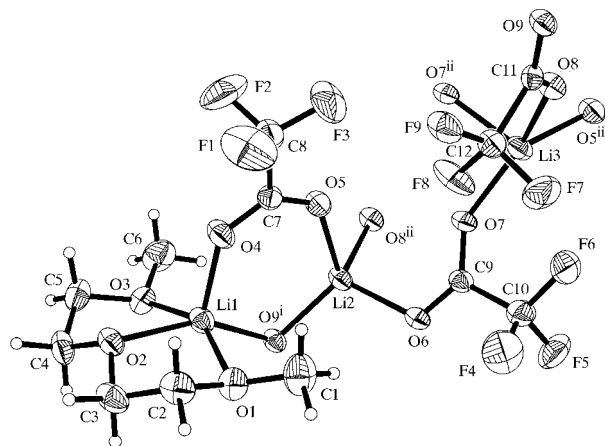


Figure 1

A view of the structure of (I), showing the Li<sup>+</sup> coordination environment and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i)  $-x, 2-y, 1-z$ ; (ii)  $1-x, 2-y, 1-z$ ].

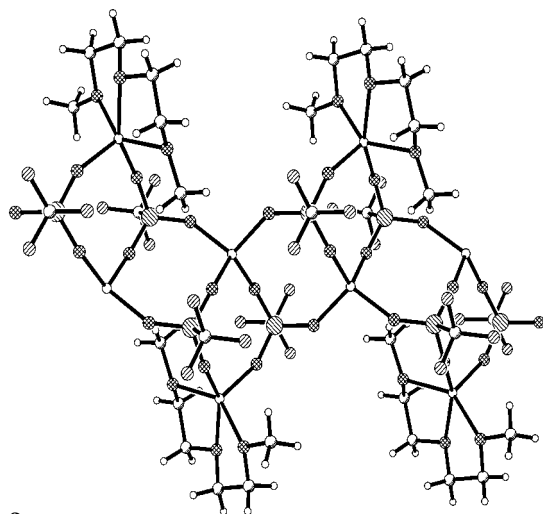
Despite the highly aggregated nature of the ions, the coordination in (I) still differs markedly from that found in crystalline  $\text{LiCF}_3\text{SO}_3$  (Tremayne *et al.*, 1992), in which four-coordinate  $\text{Li}^+$  cations are each coordinated by three  $\text{CF}_3\text{SO}_3^-$  anions. The anions are tetradentate in the crystalline  $\text{LiCF}_3\text{SO}_3$  salt, coordinated to three cations with two O atoms coordinated to the same cation.

The  $\text{Li}^+$  cations coordinated to the diglyme molecules in (I) and (II) have the same form of cationic coordination as that found in the structures of poly(ethylene oxide)<sub>3</sub>- $\text{LiCF}_3\text{SO}_3$  (Lightfoot *et al.*, 1993) and (diglyme)<sub>1</sub>- $\text{LiCF}_3\text{SO}_3$  (Rhodes & Frech, 2001). In the structure of (diglyme)<sub>1</sub>- $\text{LiCF}_3\text{SO}_3$ , the asymmetric unit contains two independent halves of two (diglyme) $\text{Li}(\text{CF}_3\text{SO}_3)_2\text{Li}(\text{diglyme})$  dimers, which have the same connectivity but slightly different geometrical parameters. Each dimer has a crystallographic inversion center at the centroid between two S atoms of the  $\text{CF}_3\text{SO}_3^-$  anions. The



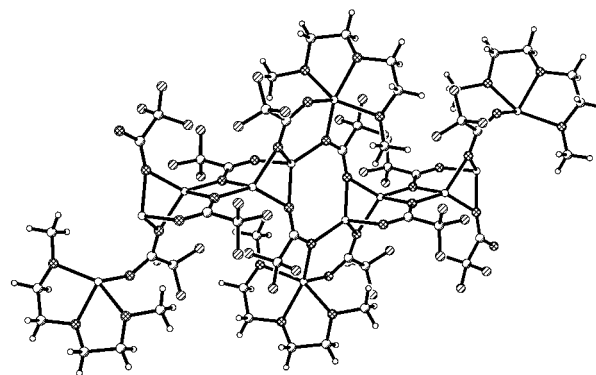
**Figure 2**

A view of the structure of (II), showing the  $\text{Li}^+$  coordination environment and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The anion  $\text{CF}_3$  group containing atom C8 is disordered over three positions of equal occupancy (not shown) around the C—C bond [symmetry codes: (i)  $3 - x, -y, 1 - z$ ; (ii)  $1 - x, y, z$ ].



**Figure 3**

A view of the packing in (I). C atoms are shown as half-shaded spheres, H atoms as open spheres, Li atoms as dotted spheres, O atoms as cross-hatched spheres, F atoms as small hatched spheres and S atoms as large hatched spheres.



**Figure 4**

A view of the packing in (II); the atom-shading scheme is the same as that used in Fig. 3.

dimers contain two five-coordinate  $\text{Li}^+$  cations, coordinated by three ether O atoms from a diglyme molecule and two O atoms from two separate  $\text{CF}_3\text{SO}_3^-$  anions. The anions are bidentate, coordinated to both  $\text{Li}^+$  cations in each dimer through two O atoms. In contrast, the  $\text{CF}_3\text{SO}_3^-$  anions in (I) are tridentate, coordinated to three different  $\text{Li}^+$  cations. In (II), the  $\text{CF}_3\text{CO}_2^-$  anions are either tri- or tetradentate, coordinated to three or four different  $\text{Li}^+$  cations.

The  $\text{Li1—O}$  bond lengths and angles in (I) and (II) (Tables 1 and 2) are similar to those found in both poly(ethylene oxide)<sub>3</sub>- $\text{LiCF}_3\text{SO}_3$  and (diglyme)<sub>1</sub>- $\text{LiCF}_3\text{SO}_3$ . The remaining four-coordinate  $\text{Li}^+$  cations in (I) and (II) are coordinated by four separate anions. The O—Li—O angles at Li2 in (I) are within  $4^\circ$  of  $109.5^\circ$  [ $106.4(2)$ – $113.0(2)^\circ$ ], indicating a regular tetrahedral geometry (Table 1). However, the O—Li—O angles at Li2 [ $86.8(1)$ – $131.2(1)^\circ$ ] and Li3 [ $86.6(1)$ – $141.9(1)^\circ$ ] in (II) indicate a highly distorted tetrahedral geometry (Table 2). The difference in anion coordination accounts for the different stoichiometries of (I) and (II). The phase diagram of the diglyme- $\text{LiCF}_3\text{CO}_2$  system indicates that a (diglyme)<sub>1</sub>- $\text{LiCF}_3\text{CO}_2$  compound also forms (Henderson, 2002).

Note that, although 1:1 mole ratio mixtures were used to prepare (I) and (II), the (diglyme)<sub>1</sub>- $\text{LiX}$  ( $X$  is  $\text{CF}_3\text{SO}_3^-$  or  $\text{CF}_3\text{CO}_2^-$ ) phases did not crystallize at 295 K, despite having melting temperatures of 320 and 302 K, respectively; single crystals of (I) and (II) formed slowly instead. The probable explanation for this is the considerable hysteresis between the crystallization and melting temperatures (Henderson, 2002) of many glyme-lithium salt phases. Some of the  $\text{Li}^+$  cations in the amorphous mixture which is formed after melting and cooling to room temperature are likely to be aggregated into solvate structures similar to those found in the reported compounds. This facilitates nucleation of (I) and (II) rather than the structures predicted thermodynamically from the phase diagrams.

## Experimental

Preparations were carried out in a dry room (<1% relative humidity).  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiCF}_3\text{CO}_2$  (Aldrich) were dried at 383 K under high vacuum for 12 h. Anhydrous diglyme [bis(2-methoxyethyl) ether; 99.5%, Aldrich] was used as received. Compounds (I) and (II) were prepared by the addition of diglyme to the salts, in 1:1 molar ratios.

The mixtures were stirred while heating to dissolve the salts. Single crystals grew slowly on standing the solutions at room temperature.

**Compound (I)**

*Crystal data*

[Li<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)]  
*M<sub>r</sub>* = 446.19  
 Triclinic, *P*<sub>1</sub><sup>̄</sup>  
*a* = 8.678 (3) Å  
*b* = 10.815 (3) Å  
*c* = 11.899 (4) Å  
 α = 67.566 (5)°  
 β = 89.831 (5)°  
 γ = 71.435 (5)°  
*V* = 969.5 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.528 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1639 reflections  
 θ = 1.9–25.1°  
 μ = 0.37 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Plate, colorless  
 0.30 × 0.20 × 0.04 mm

*Data collection*

Bruker SMART CCD-platform area-detector diffractometer  
 φ and ω scans  
 Absorption correction: multi-scan (SADABS; Blessing, 1995; Sheldrick, 2001)  
*T<sub>min</sub>* = 0.898, *T<sub>max</sub>* = 0.986  
 7068 measured reflections  
 3402 independent reflections  
 2751 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.038  
 θ<sub>max</sub> = 25.1°  
*h* = -10 → 10  
*k* = -11 → 12  
*l* = 0 → 14

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR*(*F*<sup>2</sup>) = 0.116  
*S* = 1.02  
 3402 reflections  
 246 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.5304P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.43 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.36 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

Li1–O1	2.050 (4)	Li2–O5	1.933 (4)
Li1–O2	2.113 (4)	Li2–O8	1.901 (4)
Li1–O3	2.103 (5)	Li2–O6 <sup>i</sup>	1.938 (4)
Li1–O4	2.017 (4)	Li2–O9 <sup>ii</sup>	1.939 (4)
Li1–O7	1.951 (4)		
C1–O1–C2–C3	173.9 (3)	C3–O2–C4–C5	156.8 (2)
O1–C2–C3–O2	48.5 (3)	O2–C4–C5–O3	-55.0 (3)
C2–C3–O2–C4	-172.0 (2)	C4–C5–O3–C6	-172.0 (2)

Symmetry codes: (i) 1 - *x*, 2 - *y*, 1 - *z*; (ii) -*x*, 2 - *y*, 1 - *z*.

**Compound (II)**

*Crystal data*

[Li<sub>3</sub>(C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)]  
*M<sub>r</sub>* = 494.05  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 9.545 (4) Å  
*b* = 13.871 (6) Å  
*c* = 15.589 (7) Å  
 β = 92.974 (8)°  
*V* = 2061.2 (15) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.592 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2819 reflections  
 θ = 2.9–24.8°  
 μ = 0.18 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, colorless  
 0.36 × 0.32 × 0.24 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer  
 φ and ω scans  
 Absorption correction: multi-scan (SADABS; Blessing, 1995; Sheldrick, 2001)  
*T<sub>min</sub>* = 0.878, *T<sub>max</sub>* = 0.937  
 19 973 measured reflections  
 3657 independent reflections  
 3038 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.022  
 θ<sub>max</sub> = 25.1°  
*h* = -11 → 11  
*k* = -16 → 16  
*l* = -18 → 18

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.026  
*wR*(*F*<sup>2</sup>) = 0.067  
*S* = 1.03  
 3657 reflections  
 355 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 0.5588P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.17 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.18 e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0022 (6)

**Table 2**

Selected geometric parameters (Å, °) for (II).

Li1–O1	2.105 (3)	Li2–O8 <sup>ii</sup>	1.991 (2)
Li1–O2	2.023 (2)	Li2–O9 <sup>i</sup>	1.935 (2)
Li1–O3	2.096 (3)	Li3–O5 <sup>ii</sup>	1.936 (2)
Li1–O4	1.950 (2)	Li3–O7	1.917 (2)
Li1–O9 <sup>i</sup>	2.064 (3)	Li3–O7 <sup>ii</sup>	1.981 (3)
Li2–O5	1.967 (2)	Li3–O8	2.051 (2)
Li2–O6	1.962 (2)		
C1–O1–C2–C3	-179.79 (13)	C3–O2–C4–C5	-170.93 (11)
O1–C2–C3–O2	-57.80 (14)	O2–C4–C5–O3	53.80 (14)
C2–C3–O2–C4	171.05 (11)	C4–C5–O3–C6	-179.79 (12)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) 1 - *x*, -*y*, 1 - *z*.

The H atoms were placed geometrically, with C–H distances in the range 0.98–0.99 Å, and allowed to refine riding on their parent C atoms.

For both compounds, data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT. For compound (I), program(s) used to solve structure: SHELXS97 (Sheldrick, 1997). For compound (II), program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993). For both compounds, program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Bruker, 1998); software used to prepare material for publication: SHELXTL/PC and PLATON (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1134). Additional figures are also available. Services for accessing these data are described at the back of the journal.

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