

Crystal structures of polymerized lithium chloride and dimethyl sulfoxide in the form of $\{2\text{LiCl}\cdot 3\text{DMSO}\}_n$ and $\{\text{LiCl}\cdot \text{DMSO}\}_n$

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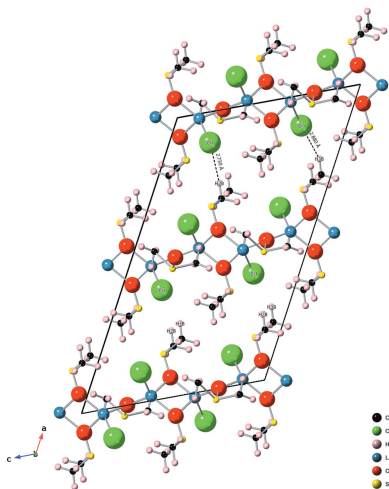
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Two novel LiCl-DMSO polymer structures were created by combining dry LiCl salt with dimethyl sulfoxide (DMSO), namely, *catena*-poly[[chloridolithium(I)]- μ -(dimethyl sulfoxide)- $\kappa^2 O:O$ -[chloridolithium(I)]-di- μ -(dimethyl sulfoxide)- $\kappa^4 O:O$], $[\text{Li}_2\text{Cl}_2(\text{C}_2\text{H}_6\text{OS})_3]_n$, and *catena*-poly[lithium(I)- μ -chlorido- μ -(dimethyl sulfoxide)- $\kappa^2 O:O$], $[\text{LiCl}(\text{C}_2\text{H}_6\text{OS})]_n$. The initial synthesized phase had very small block-shaped crystals (<0.08 mm) with monoclinic symmetry and a 2 LiCl: 3 DMSO ratio. As the solution evaporated, a second phase formed with a plate-shaped crystal morphology. After about 20 minutes, large (>0.20 mm) octahedron-shaped crystals formed. The plate crystals and the octahedron crystals are the same tetragonal structure with a 1 LiCl: 1 DMSO ratio. These structures are reported and compared to other known LiCl-solvent compounds.

1. Chemical context

Lithium salts are soluble in a wide range of solvents and are widely used in lithium-metal and lithium-ion battery applications (Bushkova *et al.*, 2017; Mauger *et al.*, 2018; Younesi *et al.*, 2015). While typically implemented as liquid electrolyte solutions, the lithium salt and solvent systems can also form complex molecular phases, including intercalating compounds (Yamada *et al.*, 2010), crystalline solvates (Ugata *et al.*, 2021), and polymeric structures (Rao *et al.*, 1984; Chivers *et al.*, 2001).

Dimethyl sulfoxide (DMSO) and lithium chloride (LiCl) are very common materials in many industries, and have each been used in novel battery systems, including solid-polymer (Voigt & van Wüllen, 2012), dual-ion (Wang *et al.*, 2022), lithium-oxygen (Togasaki *et al.*, 2016; Reddy *et al.*, 2018; Zhang *et al.*, 2021) and molten-salt electrolyte batteries (Allcorn *et al.*, 2020). Given that DMSO and water both exhibit a coordination number of four solvent molecules per cation (Megyes *et al.*, 2006; Bouazizi & Nasr, 2007), it is reasonable to hypothesize that the two solvents solvate lithium ions similarly. For Li^+ cations in binary solvent solutions of DMSO and water, the solvent molecules are analogous; there is effectively no selective solvation of Li^+ cations for either DMSO or water (Pasgreta *et al.*, 2007). Thus it is not surprising that lithium salts would form similar crystalline phases when comparing phase diagrams in pure DMSO (Kirillov *et al.*, 2015) and pure water (Perron *et al.*, 1997). Since LiCl is hydrated with 1–2 water molecules per Li^+ cation in ambient conditions (Conde, 2004; Pátek & Klomfar, 2006), it is reasonable to expect that LiCl would form similar if not

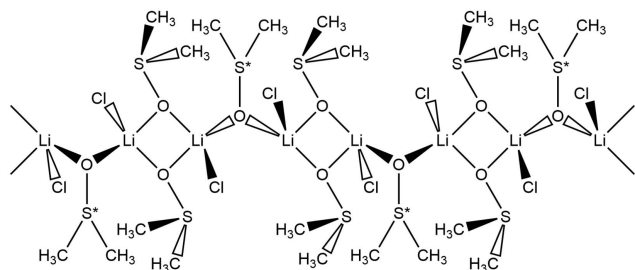


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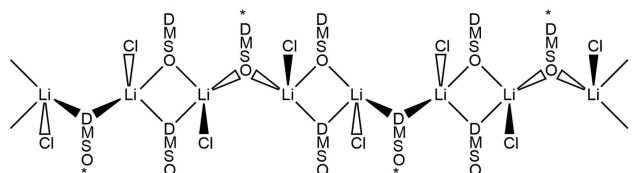
analogous solvate phases in DMSO (1–2 DMSO molecules per Li^+ cation).

Monoclinic Structure

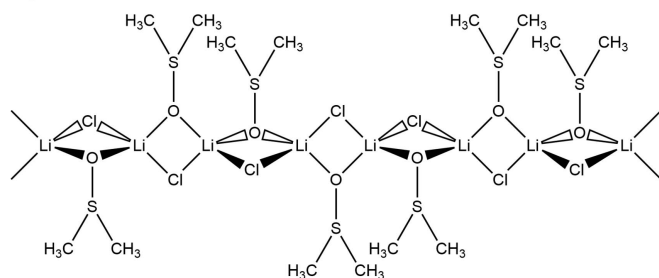


* Indicates the sulfur atom is disordered

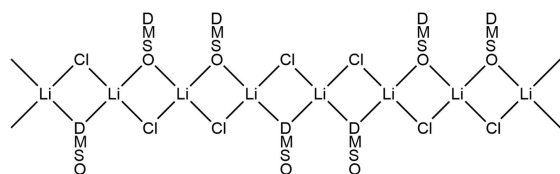
Monoclinic Structure, Simplified



Tetragonal Structure



Tetragonal Structure, Simplified



2. Synthesis and crystallization

Material samples were prepared using lithium chloride (Acros Organics, LiCl 99% anhydrous) and dimethyl sulfoxide (Sigma-Aldrich, $\text{C}_2\text{H}_6\text{OS}$ $\geq 99.9\%$ anhydrous). Before use, the LiCl was heated to 423.15 K (150°C) under vacuum to remove any trace moisture, and the sample preparation was carried out in a humidity-controlled dry room, dew point below 223.15 K (-50°C).

Dry LiCl was added to a jar of DMSO at a ratio of 5 g LiCl per 25 g DMSO, approximately twice the limit at 298.15 K (25°C) before saturation is initially observed (Xin *et al.*, 2018). As the salt tends to agglomerate quickly upon being added to the DMSO, the initial larger agglomerates were manually broken up. The jar was then sealed and the entire solution was stirred vigorously with a magnetic stir bar for 3 days. An aliquot of the sample (solids and saturated DMSO combined) was removed for analysis. During sample preparation for single crystal X-ray diffraction analysis, DMSO evaporated

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for the monoclinic structure.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1A}\cdots\text{Cl1}^{\text{i}}$	0.97 (1)	2.98 (4)	3.569 (3)	120 (3)
$\text{C1}-\text{H1B}\cdots\text{Cl1}^{\text{ii}}$	0.97 (1)	2.79 (2)	3.690 (3)	156 (3)
$\text{C2}-\text{H2A}\cdots\text{Cl1}^{\text{iii}}$	0.98	2.71	3.680 (3)	169
$\text{C2}-\text{H2B}\cdots\text{Cl1}^{\text{iv}}$	0.98	2.73	3.632 (3)	153
$\text{C3}-\text{H3B}\cdots\text{Cl1}^{\text{iv}}$	0.98	2.88	3.752 (3)	149

Symmetry codes: (i) $-x + 1, y - 1, -z + \frac{1}{2}$; (ii) $x, -y + 1, z - \frac{1}{2}$; (iii) $-x + 1, y, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

from the sample aliquot, resulting in a second, likely metastable, phase with different crystal morphology.

3. Structural Commentary

Monoclinic Crystals

The initial crystals synthesized as described in the previous section are small (<0.08 mm), block-shaped, and have monoclinic symmetry $C2/c$. The polymer has a 2 LiCl : 3 DMSO

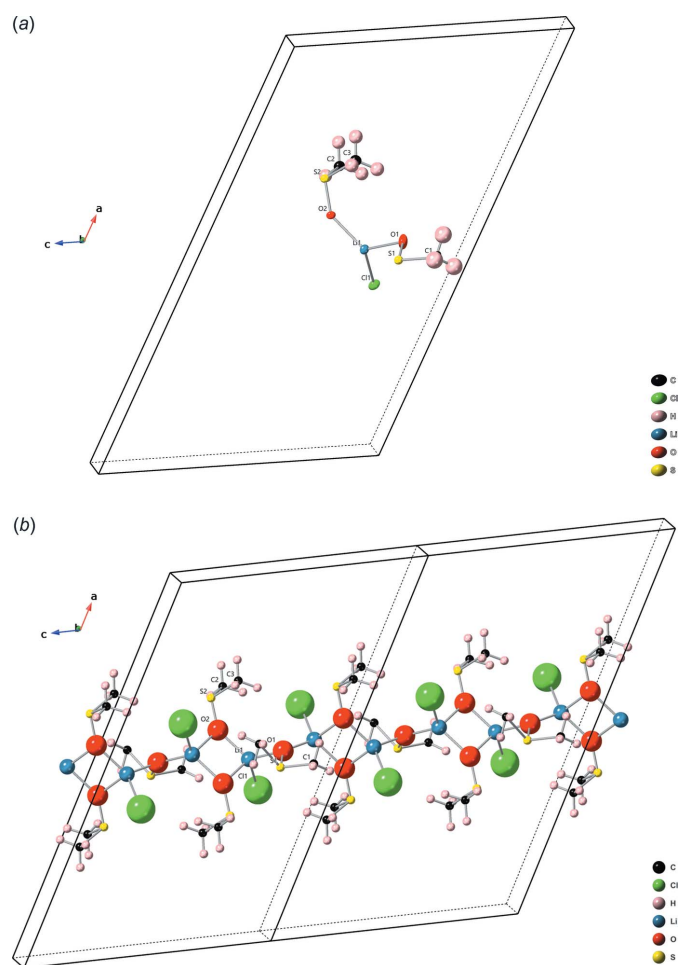


Figure 1
Monoclinic structure: asymmetric unit (a) and polymeric chain view (b). The repeating unit of the polymer has four LiCl and six DMSO. The sulfur atom of the DMSO is disordered across two positions. Only one position is shown.

ratio, and the repeating unit is composed of four LiCl, and six DMSO, see Fig. 1 and Scheme.

The polymers appear to be held together by hydrogen bonding, see Table 1 and packing diagram Fig. 2. The most notable bond is between Cl1 and H2B (2.730 Å), where the Cl atom on one polymer chain is connected to one of the hydrogen atoms on one of the methyl groups of the non-disordered DMSO molecule of another polymer chain. There is likely some hydrogen bond contribution from the adjacent H3B, which is located on the other methyl group of the same DMSO molecule (hydrogen-bond length 2.88 Å). If the disordered DMSO molecule contributes to hydrogen bonding between polymer chains, it would be through hydrogen H1A and Cl1, however this bond is very long [2.98 (3) Å]. The other values in the table represent hydrogen bonding between a DMSO molecule and a Cl atom along the same polymer chain.

Tetragonal Crystals

The second crystal phase formed during sample preparation as DMSO evaporated. At first, plate-shaped crystals appeared among the smaller block-shaped crystals. As more time passed (~20 minutes), much larger (0.2–0.4 mm) octahedron-shaped crystals formed. The plate crystals and the octahedron crystals are the same tetragonal $I4_1/a$ structure with a 1 LiCl : 1 DMSO ratio. The repeating unit has four LiCl, and four DMSO. The

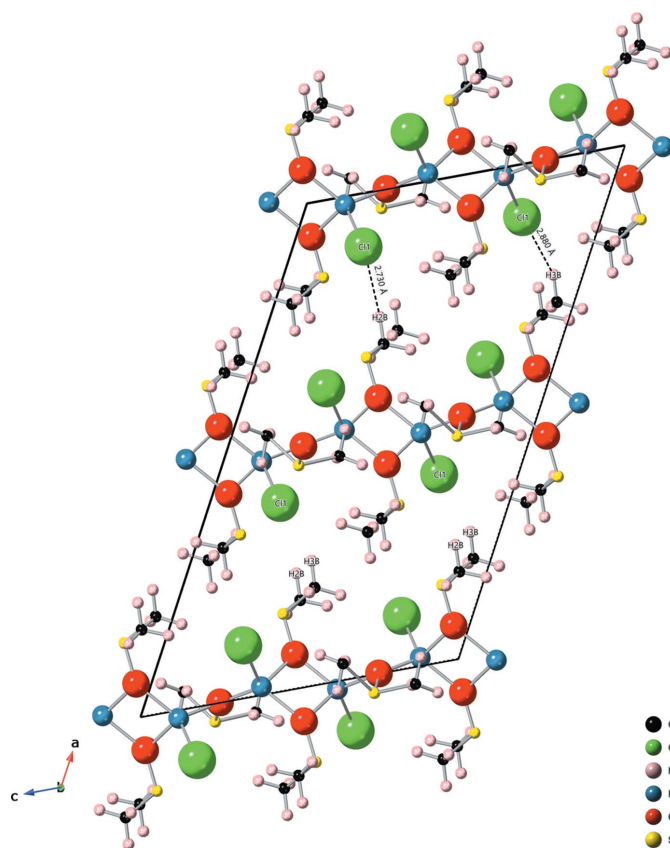


Figure 2
Monoclinic structure: packing diagram. The structure is held together by hydrogen bonding. The hydrogen bonds between Cl1 and H2B as well as Cl1 and H3B are shown.

Table 2
Hydrogen-bond geometry (Å, °) for the tetragonal structure.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1–H1B \cdots Cl1 ⁱ	0.98 (2)	2.95 (2)	3.821 (2)	148 (2)
C2–H2A \cdots Cl1 ⁱⁱ	0.95 (2)	2.84 (2)	3.768 (2)	165 (2)
C2–H2C \cdots Cl1 ⁱ	0.96 (2)	2.83 (2)	3.716 (2)	153 (2)

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$.

DMSO molecules are not disordered in this structure, see Fig. 3 and Scheme.

As with the monoclinic structure, the tetragonal structure is composed of polymer chains held together by hydrogen bonding, see Table 2 and the packing diagram Fig. 4. The Cl1 of one chain is linked to the DMSO of another chain through H2A [2.84 (2) Å] and H2C [2.83 (2) Å]. There may be some

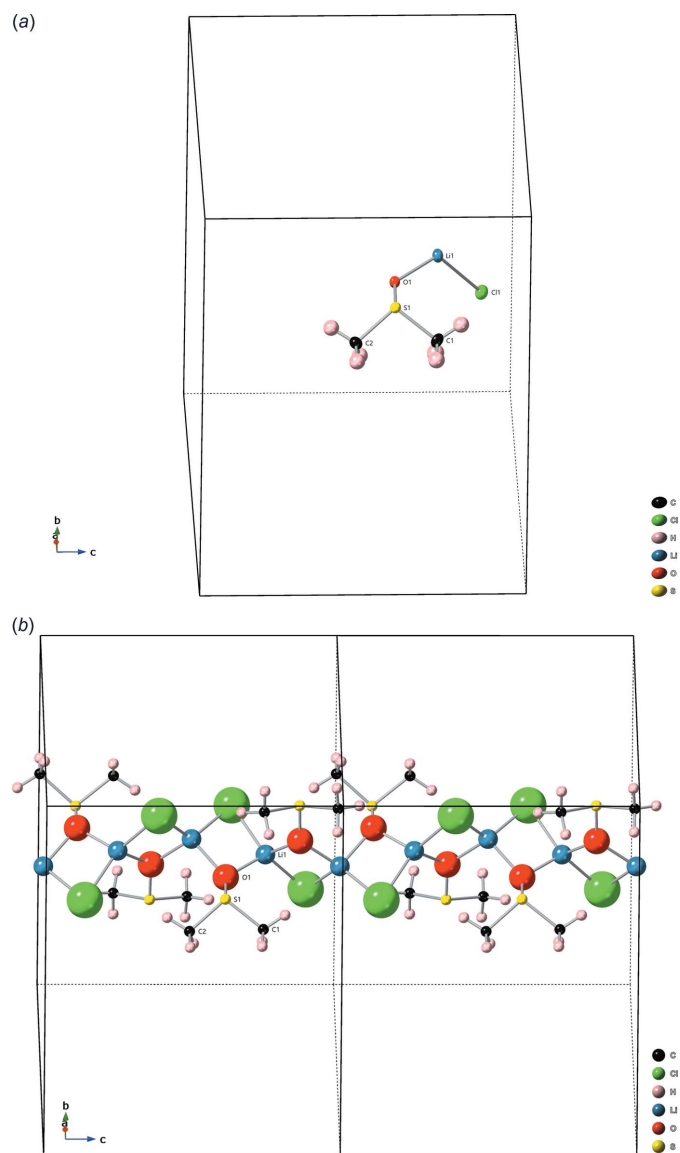


Figure 3
Tetragonal structure: asymmetric unit (a) and polymeric chain view (b). The repeating unit of the polymer has four LiCl and four DMSO. The DMSO molecules in this structure are not disordered.

Table 3
Experimental details.

	Monoclinic	Tetragonal
Crystal data		
Chemical formula	[Li ₂ Cl ₂ (C ₂ H ₆ OS) ₃]	[LiCl(C ₂ H ₆ OS)]
<i>M_r</i>	319.16	120.52
Crystal system, space group	Monoclinic, <i>C2/c</i>	Tetragonal, <i>I4₁/a</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.2841 (17), 7.6436 (7), 11.5335 (10)	14.2411 (14), 14.2411 (14), 10.8809 (16)
α , β , γ (°)	90, 118.315 (5), 90	90, 90, 90
<i>V</i> (Å ³)	1496.6 (2)	2206.7 (5)
<i>Z</i>	4	16
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α
μ (mm ⁻¹)	7.72	8.49
Crystal size (mm)	0.07 × 0.07 × 0.05	0.4 × 0.4 × 0.4
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.639, 0.754	0.513, 0.754
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	10606, 1417, 1166	8174, 1072, 1030
<i>R_{int}</i>	0.064	0.047
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.610	0.618
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.081, 1.09	0.028, 0.073, 1.07
No. of reflections	1417	1072
No. of parameters	92	79
No. of restraints	68	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.46, -0.39	0.32, -0.37

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

contribution from H1B, though the bond is much longer [2.95 (2) Å].

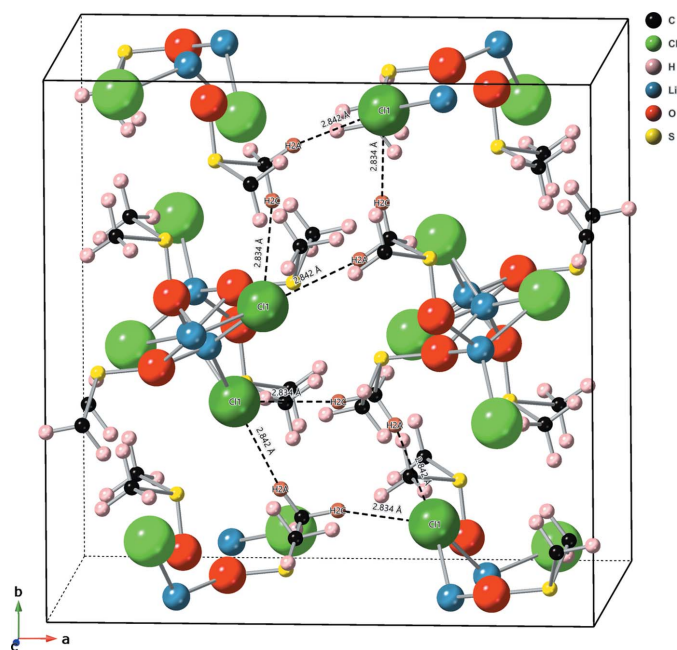


Figure 4
Tetragonal structure: packing diagram. The structure is held together by hydrogen bonding. The hydrogen bonds between Cl1 and H2A and Cl1 and H2C are shown. The atoms involved in hydrogen bonding are darkened for clarity.

4. Database Survey

After the structures were solved, a search was performed on the Cambridge Structural Database (CSD, version 5.43, November 2021; Groom *et al.*, 2016). There were only two results with the relevant chemistry, and neither had DMSO. One was a LiCl sulfolane adduct (SIWFOT; Harvey *et al.*, 1991), and the other was a crown ether complex (XEGBIX; Reuter *et al.*, 2017). These two LiCl–DMSO structures are novel, and other phases likely exist in the LiCl–DMSO system as a function of temperature, analogous to the LiCl–H₂O system (Perron *et al.*, 1997). An extensive list of LiCl structures with various other ligands can be found in Chivers *et al.* (2001).

5. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. One of the DMSO molecules on the monoclinic structure is disordered. The two positions of the sulfur atom show a C₂ symmetry-related disorder about the oxygen atom in the *b*-axis direction of the unit cell. An attempt was made to model the disorder using a lower space group (*Cc*); however, the refinement was unstable. Without the ability to use a PART instruction, the DMSO molecule was fixed to an occupancy of 0.5. The hydrogen atoms on the disordered DMSO molecule were placed manually. For the monoclinic structure, all H atoms were refined with *U*_{iso}(H) =

$1.5U_{eq}(C)$. Bond-length restraints of $0.98 \pm 0.02 \text{ \AA}$ were applied to the H atoms on C2 and C3.

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supporting information

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

catena-Poly[[chloridolithium(I)]- μ -(dimethyl sulfoxide)- $\kappa^2\text{O}$:O-[chloridolithium(I)]-di- μ -(dimethyl sulfoxide)- $\kappa^4\text{O}$:O] (Monoclinic)

Crystal data

$[\text{Li}_2\text{Cl}_2(\text{C}_2\text{H}_6\text{OS})_3]$
 $M_r = 319.16$
 Monoclinic, *C2/c*
 $a = 19.2841$ (17) Å
 $b = 7.6436$ (7) Å
 $c = 11.5335$ (10) Å
 $\beta = 118.315$ (5)°
 $V = 1496.6$ (2) Å³
 $Z = 4$

$F(000) = 664$
 $D_x = 1.416$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
 Cell parameters from 4022 reflections
 $\theta = 5.2\text{--}71.2^\circ$
 $\mu = 7.72$ mm⁻¹
 $T = 100$ K
 Block, colourless
 $0.07 \times 0.07 \times 0.05$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.639$, $T_{\max} = 0.754$
 10606 measured reflections

1417 independent reflections
 1166 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\max} = 70.0^\circ$, $\theta_{\min} = 5.2^\circ$
 $h = -22 \rightarrow 23$
 $k = -9 \rightarrow 9$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.081$
 $S = 1.09$
 1417 reflections
 92 parameters
 68 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0023P)^2 + 6.8363P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Li1	0.4831 (3)	0.5661 (7)	0.3715 (4)	0.0215 (10)	
Cl1	0.39011 (4)	0.78167 (9)	0.26503 (6)	0.02346 (19)	
O1	0.500000	0.4171 (4)	0.250000	0.0231 (6)	
S1	0.46168 (7)	0.23074 (17)	0.24491 (12)	0.0150 (3)	0.5
C1	0.46522 (18)	0.1205 (4)	0.1177 (3)	0.0227 (6)	
H1A	0.463 (2)	−0.006 (2)	0.125 (4)	0.052 (12)*	
H1B	0.439 (2)	0.178 (5)	0.033 (2)	0.052 (12)*	
H1C	0.519 (2)	0.121 (12)	0.129 (9)	0.21 (4)*	
O2	0.57073 (10)	0.5856 (3)	0.55161 (17)	0.0184 (4)	
S2	0.65940 (4)	0.60785 (9)	0.63468 (6)	0.01629 (18)	
C2	0.68091 (16)	0.8173 (4)	0.5918 (3)	0.0207 (6)	
H2A	0.659005	0.824918	0.496007	0.031*	
H2B	0.738110	0.833830	0.633975	0.031*	
H2C	0.657431	0.908521	0.621951	0.031*	
C3	0.70219 (17)	0.4751 (4)	0.5580 (3)	0.0229 (6)	
H3A	0.694545	0.351352	0.571155	0.034*	
H3B	0.758674	0.500205	0.597297	0.034*	
H3C	0.676854	0.500799	0.463501	0.034*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.017 (2)	0.032 (3)	0.014 (2)	−0.001 (2)	0.0064 (18)	−0.0028 (19)
Cl1	0.0195 (3)	0.0272 (4)	0.0174 (3)	−0.0028 (3)	0.0037 (3)	0.0043 (3)
O1	0.0408 (17)	0.0139 (13)	0.0175 (14)	0.000	0.0162 (13)	0.000
S1	0.0136 (6)	0.0169 (6)	0.0141 (6)	−0.0003 (5)	0.0063 (5)	−0.0001 (5)
C1	0.0275 (16)	0.0185 (15)	0.0152 (14)	−0.0019 (13)	0.0045 (13)	−0.0008 (11)
O2	0.0111 (9)	0.0284 (11)	0.0139 (9)	−0.0011 (8)	0.0046 (7)	0.0003 (8)
S2	0.0125 (3)	0.0213 (4)	0.0138 (3)	−0.0014 (3)	0.0052 (3)	0.0013 (3)
C2	0.0189 (14)	0.0214 (15)	0.0198 (14)	−0.0024 (11)	0.0074 (12)	0.0001 (11)
C3	0.0202 (14)	0.0260 (16)	0.0238 (15)	−0.0008 (12)	0.0114 (12)	−0.0019 (12)

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

Li1—Li1 ⁱ	3.162 (9)	C1—H1A	0.972 (14)
Li1—Li1 ⁱⁱ	2.899 (9)	C1—H1B	0.967 (14)
Li1—Cl1	2.313 (5)	C1—H1C	0.974 (15)
Li1—O1	1.949 (5)	O2—S2	1.5219 (18)
Li1—S1	2.881 (5)	S2—C2	1.782 (3)

Li1—O2 ⁱⁱ	2.021 (5)	S2—C3	1.785 (3)
Li1—O2	1.966 (5)	C2—H2A	0.9800
Li1—S2 ⁱⁱ	3.024 (5)	C2—H2B	0.9800
O1—S1	1.593 (3)	C2—H2C	0.9800
O1—S1 ⁱ	1.593 (3)	C3—H3A	0.9800
S1—S1 ⁱ	1.426 (2)	C3—H3B	0.9800
S1—C1	1.721 (3)	C3—H3C	0.9800
S1—C1 ⁱ	1.758 (3)		
Li1 ⁱⁱ —Li1—Li1 ⁱ	149.9 (3)	S1 ⁱ —S1—O1	63.41 (6)
Li1 ⁱⁱ —Li1—S2 ⁱⁱ	68.36 (17)	S1 ⁱ —S1—C1 ⁱ	64.48 (13)
Cl1—Li1—Li1 ⁱⁱ	122.2 (3)	S1 ⁱ —S1—C1	67.14 (13)
Cl1—Li1—Li1 ⁱ	87.91 (16)	C1 ⁱ —S1—Li1	96.24 (14)
Cl1—Li1—S1	118.43 (18)	C1—S1—Li1	144.41 (15)
Cl1—Li1—S2 ⁱⁱ	80.40 (13)	C1—S1—C1 ⁱ	101.25 (18)
O1—Li1—Li1 ⁱⁱ	119.9 (3)	S1—C1—S1 ⁱ	48.38 (11)
O1—Li1—Li1 ⁱ	35.76 (16)	S1 ⁱ —C1—H1A	117 (2)
O1—Li1—Cl1	112.8 (2)	S1—C1—H1A	113 (2)
O1—Li1—S1	31.64 (11)	S1—C1—H1B	115 (2)
O1—Li1—O2	116.8 (2)	S1 ⁱ —C1—H1B	120 (2)
O1—Li1—O2 ⁱⁱ	106.0 (3)	S1—C1—H1C	111 (5)
O1—Li1—S2 ⁱⁱ	100.72 (19)	S1 ⁱ —C1—H1C	62 (5)
S1—Li1—Li1 ⁱ	65.90 (10)	H1A—C1—H1B	121 (3)
S1—Li1—Li1 ⁱⁱ	96.7 (2)	H1A—C1—H1C	95 (5)
S1—Li1—S2 ⁱⁱ	71.72 (12)	H1B—C1—H1C	98 (5)
O2 ⁱⁱ —Li1—Li1 ⁱⁱ	42.59 (14)	Li1—O2—Li1 ⁱⁱ	93.3 (2)
O2—Li1—Li1 ⁱ	120.1 (3)	S2—O2—Li1 ⁱⁱ	116.46 (16)
O2—Li1—Li1 ⁱⁱ	44.10 (13)	S2—O2—Li1	145.04 (17)
O2 ⁱⁱ —Li1—Li1 ⁱ	138.89 (18)	O2—S2—Li1 ⁱⁱ	36.75 (11)
O2 ⁱⁱ —Li1—Cl1	102.2 (2)	O2—S2—C2	105.41 (12)
O2—Li1—Cl1	124.6 (2)	O2—S2—C3	105.66 (12)
O2 ⁱⁱ —Li1—S1	74.44 (17)	C2—S2—Li1 ⁱⁱ	135.83 (14)
O2—Li1—S1	116.6 (2)	C2—S2—C3	98.65 (14)
O2—Li1—O2 ⁱⁱ	86.7 (2)	C3—S2—Li1 ⁱⁱ	111.54 (14)
O2 ⁱⁱ —Li1—S2 ⁱⁱ	26.78 (8)	S2—C2—H2A	109.5
O2—Li1—S2 ⁱⁱ	111.96 (19)	S2—C2—H2B	109.5
S2 ⁱⁱ —Li1—Li1 ⁱ	123.1 (2)	S2—C2—H2C	109.5
Li1 ⁱ —O1—Li1	108.5 (3)	H2A—C2—H2B	109.5
S1—O1—Li1 ⁱ	136.79 (16)	H2A—C2—H2C	109.5
S1 ⁱ —O1—Li1 ⁱ	108.45 (16)	H2B—C2—H2C	109.5
S1—O1—Li1	108.45 (16)	S2—C3—H3A	109.5
S1 ⁱ —O1—Li1	136.79 (16)	S2—C3—H3B	109.5
S1—O1—S1 ⁱ	53.18 (13)	S2—C3—H3C	109.5
O1—S1—Li1	39.92 (10)	H3A—C3—H3B	109.5
O1—S1—C1 ⁱ	103.64 (12)	H3A—C3—H3C	109.5
O1—S1—C1	105.29 (13)	H3B—C3—H3C	109.5
S1 ⁱ —S1—Li1	93.68 (11)		

Li1 ⁱ —O1—S1—Li1	-147.5 (2)	Li1—O2—S2—C2	63.5 (4)
Li1 ⁱ —O1—S1—S1 ⁱ	77.3 (2)	Li1 ⁱⁱ —O2—S2—C2	-151.0 (2)
Li1—O1—S1—S1 ⁱ	-135.24 (17)	Li1 ⁱⁱ —O2—S2—C3	105.2 (2)
Li1 ⁱ —O1—S1—C1 ⁱ	129.2 (2)	Li1—O2—S2—C3	-40.4 (4)
Li1—O1—S1—C1	170.72 (19)	O1—S1—C1—S1 ⁱ	51.77 (9)
Li1 ⁱ —O1—S1—C1	23.3 (3)	S1 ⁱ —O1—S1—Li1	135.24 (17)
Li1—O1—S1—C1 ⁱ	-83.35 (19)	S1 ⁱ —O1—S1—C1 ⁱ	51.89 (13)
Li1—S1—C1—S1 ⁱ	62.0 (2)	S1 ⁱ —O1—S1—C1	-54.04 (13)
Li1—O2—S2—Li1 ⁱⁱ	-145.5 (3)	C1 ⁱ —S1—C1—S1 ⁱ	-55.91 (15)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots Cl1 ⁱⁱⁱ	0.97 (1)	2.98 (4)	3.569 (3)	120 (3)
C1—H1B \cdots Cl1 ^{iv}	0.97 (1)	2.79 (2)	3.690 (3)	156 (3)
C2—H2A \cdots Cl1 ⁱ	0.98	2.71	3.680 (3)	169
C2—H2B \cdots Cl1 ^v	0.98	2.73	3.632 (3)	153
C3—H3B \cdots Cl1 ^v	0.98	2.88	3.752 (3)	149

Symmetry codes: (i) $-x+1, y, -z+1/2$; (iii) $-x+1, y-1, -z+1/2$; (iv) $x, -y+1, z-1/2$; (v) $x+1/2, -y+3/2, z+1/2$.

catena-Poly[lithium(I)- μ -chlorido- μ -(dimethyl sulfoxide)- κ^2 O:O] (Tetragonal)

Crystal data

[LiCl(C₂H₆OS)]

$M_r = 120.52$

Tetragonal, $I4_1/a$

$a = 14.2411$ (14) \AA

$c = 10.8809$ (16) \AA

$V = 2206.7$ (5) \AA^3

$Z = 16$

$F(000) = 992$

$D_x = 1.451$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ \AA

Cell parameters from 6535 reflections

$\theta = 4.4\text{--}72.3^\circ$

$\mu = 8.49$ mm⁻¹

$T = 100$ K

Octahedron, clear colourless

$0.4 \times 0.4 \times 0.4$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.513$, $T_{\max} = 0.754$

8174 measured reflections

1072 independent reflections

1030 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 72.3^\circ$, $\theta_{\min} = 5.1^\circ$

$h = -17 \rightarrow 16$

$k = -16 \rightarrow 17$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.073$

$S = 1.07$

1072 reflections

79 parameters

0 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.762P]$

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

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

$\Delta\rho_{\max} = 0.32$ e \AA^{-3}

$\Delta\rho_{\min} = -0.37$ e \AA^{-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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.81811 (3)	0.36163 (2)	0.89755 (3)	0.02090 (17)
S1	0.58855 (3)	0.44534 (2)	0.62126 (3)	0.01513 (16)
O1	0.69499 (7)	0.45632 (8)	0.62414 (8)	0.0182 (3)
C1	0.56163 (11)	0.37206 (12)	0.74923 (14)	0.0238 (3)
H1A	0.6017 (15)	0.3177 (14)	0.7468 (19)	0.035 (5)*
H1B	0.4949 (14)	0.3561 (14)	0.7438 (18)	0.032 (5)*
H1C	0.5707 (14)	0.4087 (14)	0.822 (2)	0.030 (5)*
C2	0.56716 (10)	0.36370 (11)	0.50047 (14)	0.0194 (3)
H2A	0.6049 (14)	0.3099 (14)	0.5150 (18)	0.030 (5)*
H2B	0.5842 (13)	0.3952 (14)	0.425 (2)	0.029 (5)*
H2C	0.5011 (14)	0.3503 (14)	0.5012 (18)	0.030 (5)*
Li1	0.77950 (17)	0.48024 (16)	0.7596 (2)	0.0185 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0232 (2)	0.0197 (2)	0.0198 (2)	0.00734 (14)	0.00006 (13)	0.00281 (13)
S1	0.0163 (2)	0.0145 (2)	0.0145 (2)	-0.00053 (13)	0.00054 (12)	0.00014 (11)
O1	0.0173 (6)	0.0243 (6)	0.0128 (5)	-0.0070 (4)	-0.0005 (3)	0.0004 (4)
C1	0.0222 (8)	0.0307 (9)	0.0184 (8)	-0.0065 (7)	0.0026 (6)	0.0052 (6)
C2	0.0176 (7)	0.0212 (7)	0.0193 (7)	-0.0011 (6)	-0.0023 (5)	-0.0025 (6)
Li1	0.0216 (12)	0.0206 (12)	0.0133 (10)	0.0025 (10)	-0.0006 (9)	-0.0006 (9)

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

Cl1—Li1	2.326 (2)	C1—H1B	0.98 (2)
Cl1—Li1 ⁱ	2.336 (2)	C1—H1C	0.96 (2)
S1—O1	1.5241 (11)	C2—H2A	0.95 (2)
S1—C1	1.7819 (15)	C2—H2B	0.97 (2)
S1—C2	1.7810 (15)	C2—H2C	0.96 (2)
O1—Li1 ⁱⁱ	1.943 (3)	Li1—Li1 ⁱ	2.8126 (10)
O1—Li1	1.933 (3)	Li1—Li1 ⁱⁱ	2.8127 (10)
C1—H1A	0.96 (2)		
Li1—Cl1—Li1 ⁱ	74.22 (7)	H2A—C2—H2C	113.1 (18)
O1—S1—C1	104.95 (7)	H2B—C2—H2C	110.1 (16)
O1—S1—C2	104.61 (6)	Cl1—Li1—Cl1 ⁱⁱ	124.69 (11)
C2—S1—C1	99.06 (8)	Cl1 ⁱⁱ —Li1—Li1 ⁱ	134.17 (10)
S1—O1—Li1	130.77 (9)	Cl1—Li1—Li1 ⁱⁱ	144.79 (11)

S1—O1—Li1 ⁱⁱ	125.94 (9)	Cl1 ⁱⁱ —Li1—Li1 ⁱⁱ	52.72 (8)
Li1—O1—Li1 ⁱⁱ	93.06 (8)	Cl1—Li1—Li1 ⁱ	53.05 (7)
S1—C1—H1A	108.8 (12)	O1 ⁱ —Li1—Cl1	96.36 (10)
S1—C1—H1B	107.3 (12)	O1 ⁱ —Li1—Cl1 ⁱⁱ	113.41 (11)
S1—C1—H1C	107.3 (12)	O1—Li1—Cl1 ⁱⁱ	96.30 (10)
H1A—C1—H1B	112.8 (18)	O1—Li1—Cl1	120.75 (12)
H1A—C1—H1C	112.5 (17)	O1—Li1—O1 ⁱ	104.58 (12)
H1B—C1—H1C	107.9 (16)	O1—Li1—Li1 ⁱ	124.99 (13)
S1—C2—H2A	107.9 (12)	O1 ⁱ —Li1—Li1 ⁱ	43.34 (7)
S1—C2—H2B	106.4 (12)	O1 ⁱ —Li1—Li1 ⁱⁱ	117.22 (12)
S1—C2—H2C	107.0 (12)	O1—Li1—Li1 ⁱⁱ	43.60 (6)
H2A—C2—H2B	111.9 (16)	Li1 ⁱ —Li1—Li1 ⁱⁱ	159.29 (10)
C1—S1—O1—Li1 ⁱⁱ	-179.33 (12)	C2—S1—O1—Li1 ⁱⁱ	76.90 (13)
C1—S1—O1—Li1	-43.92 (15)	C2—S1—O1—Li1	-147.69 (13)

Symmetry codes: (i) $y+1/4, -x+5/4, z+1/4$; (ii) $-y+5/4, x-1/4, z-1/4$.

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>
C1—H1B \cdots Cl1 ⁱⁱⁱ	0.98 (2)	2.95 (2)	3.821 (2)	148 (2)
C2—H2A \cdots Cl1 ^{iv}	0.95 (2)	2.84 (2)	3.768 (2)	165 (2)
C2—H2C \cdots Cl1 ⁱⁱⁱ	0.96 (2)	2.83 (2)	3.716 (2)	153 (2)

Symmetry codes: (iii) $x-1/2, y, -z+3/2$; (iv) $-x+3/2, -y+1/2, -z+3/2$.