



LiNa₃(SO₄)₂·6H₂O: a lithium double salt causing trouble in the industrial conversion of Li₂SO₄ into LiOH

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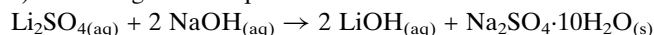
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Lithium trisodium bis(sulfate) hexahydrate, LiNa₃(SO₄)₂·6H₂O was crystallized from aqueous solution at 298 K and the structure solved at different temperatures between 90 and 293 K. The structure is isomorphic with the corresponding molybdate and selenate double salt hydrate. It belongs to the non-centrosymmetric trigonal space group *R3c* (161). The temperature dependence of the lattice parameters has been determined. Further characterization by powder XRD and thermal analysis is reported.

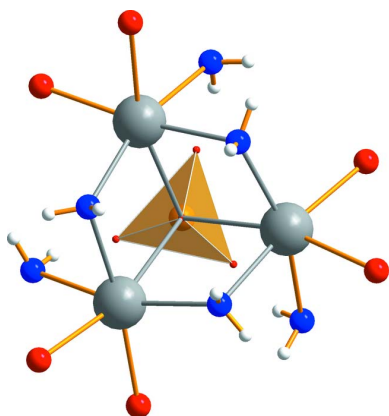
1. Chemical context

In the presently preferred process of LiOH production for batteries, an aqueous Li₂SO₄ solution is reacted with NaOH at temperatures well below 273 K (mostly at 268 K) for separating sodium sulfate in the form of its decahydrate (Glauber salt) according to the equation



The sodium sulfate hydrate is removed and from the remaining solution, water is evaporated to crystallize LiOH·H₂O. However, during cooling the solution from ambient temperature, the solution passes the stability field of LiNa₃(SO₄)₂·6H₂O, which extends from 271.3 to 321 K (Sohr *et al.*, 2017). Once formed, it will not disappear on further cooling. Rapid and reliable detection of its presence or absence by means of XRD is important. A powder diffraction pattern is available from the PDF database (Powder Diffraction File 33-1258, International Center for Diffraction Data), but no conclusive comment is attached regarding the conditions under which the material was obtained and prepared for powder XRD. It is known that the material loses its water of crystallization very easily. Therefore, in their careful thermodynamic study of the system Li₂SO₄–Na₂SO₄–H₂O at 298 K, Filippov & Kalinkin (1989) did not make an attempt to isolate the double salt hydrate because of instability. Ji *et al.* (2015) include a figure of the PXRD pattern, but only in a mixture with anhydrous LiNaSO₄. The growth of crystals under defined conditions and deriving the PXRD pattern from single-crystal structure analysis could resolve doubts about the PXRD pattern.

LiNa₃(SO₄)₂·6H₂O was first crystallized by Mitscherlich (1843) and later, preparative conditions were specified (Scacchi, 1867). Early crystallographic characterization is summarized by Groth (1908), where the cited paper of Traube (1894) is of particular interest, since he determined the correct



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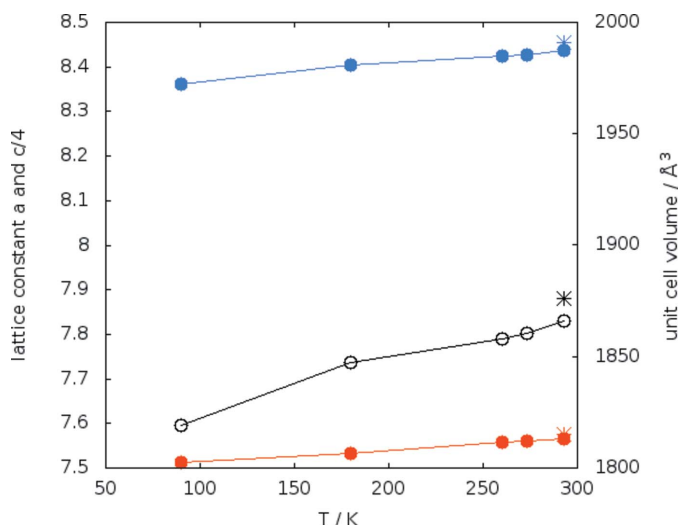


Figure 1
Variation of lattice parameters with temperature; *a* axis in red, *c* axis in blue, values divided by four, volume shown in black; circles: from single-crystal measurements, stars: data from powder X-ray measurement: $a = 8.4552(7) \text{ \AA}$, $c = 30.3032(3) \text{ \AA}$, $V = 1876.18 \text{ \AA}^3$.

polar point group $3m$ for this compound and the isomorphous compounds $\text{LiNa}_3(\text{MO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $M = \text{S, Se, Mo, Cr}$. Even a mixed compound $\text{LiNa}_3\{(\text{SO}_4)_{0.5}(\text{CrO}_4)_{0.5}\}$ was described within this series. A first crystal structure of the molybdate was published by Klevtsova *et al.* (1988). Later, Kaminskii and co-workers grew large crystals of the molybdate (Kaminskii *et al.*, 2009) and selenate (Kaminskii *et al.*, 2007) for studies on the non-linear optical effects of the materials, where they also re-determined and refined the crystal structures at ambient temperature, but without discussion of structural details.

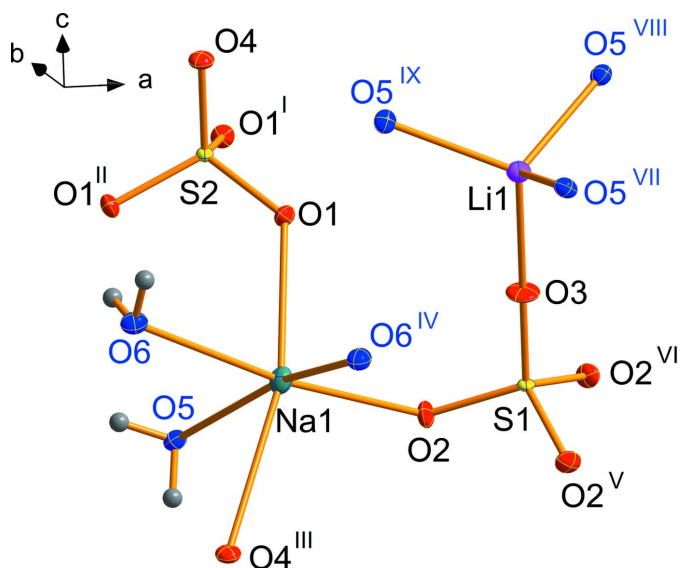


Figure 2
Asymmetric unit plus bonds. Ellipsoids are drawn at the 50% level. Symmetry codes: (I) $1 - y, 1 + x - y, z$; (II) $-y - y, 1 - x, z$; (III) $-\frac{1}{3} - x + y, -\frac{2}{3} + y, -\frac{1}{6} + z$; (IV) $-x + y, -x, z$; (V) $1 - y, x - y, z$; (VI) $1 - x + y, 1 - x, z$; (VII) $\frac{1}{3} - x + y, -\frac{1}{3} + y, \frac{1}{6} + z$; (VIII) $\frac{4}{3} - y, \frac{2}{3} - x, \frac{1}{6} + z$; (IX) $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{1}{6} + z$.

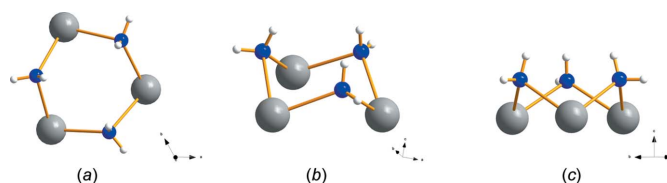


Figure 3
The trimeric unit $\text{Na}_3(\text{H}_2\text{O})_3$ viewing from different directions (*a*, *b* and *c*).

2. Structural commentary

Single-crystal structure determination was performed at five temperatures between 90 and 293 K. At all temperatures, the structure could be solved in the polar space group $R3c$ H (161). The cell parameters varied continuously with temperature (Table 1 and Fig. 1). Thus, the results confirm the isomorphism to the molybdate $\text{LiNa}_3(\text{MoO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Kaminskii *et al.*, 2009) and no structural change within the investigated temperature range. Fig. 2 shows the asymmetric unit completed with atoms to visualize the coordination of sodium, lithium and sulfur. There is only one crystallographically distinguishable sodium and lithium position, but two for sulfur. Sodium is surrounded by six oxygen atoms, three belong to water molecules (blue) and the remaining three to sulfate groups. The distance of 2.639 \AA between Na1 and O4 is quite long. Also, the angle $\text{O1}-\text{Na1}-\text{O4}$ of 165° deviates considerably from 180° . However, in a first approximation the environment of sodium atoms can be described as a distorted octahedron. The water molecules with O6 bridge three sodium ions to a trimeric unit as shown in Fig. 3. The trimers look like cyclohexane rings (Fig. 3*b*) in a chair conformation with the water molecules on the upper three points (Fig. 3*c*).

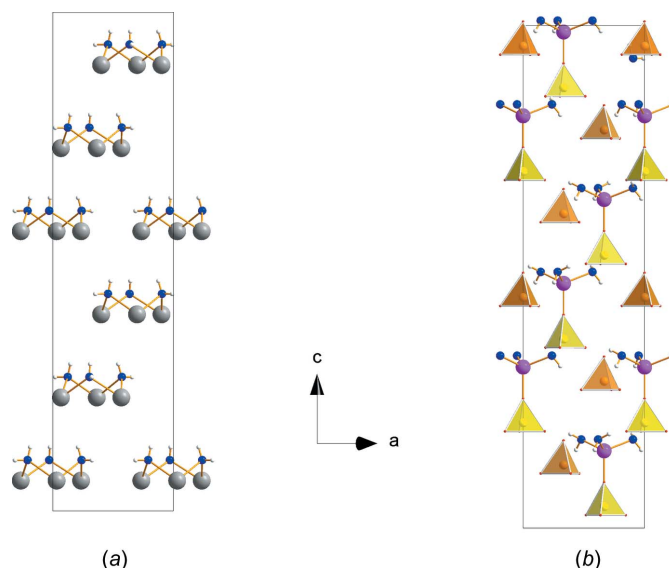


Figure 4
Stacking of (*a*) the trimeric $\text{Na}_3(\text{H}_2\text{O})_3$ and (*b*) the $\text{Li}(\text{H}_2\text{O})_3(\text{SO}_4)$ units along the *c* axis within a unit cell. Additional SO_4 groups with the S2 sulfur atom are shown (dark yellow).

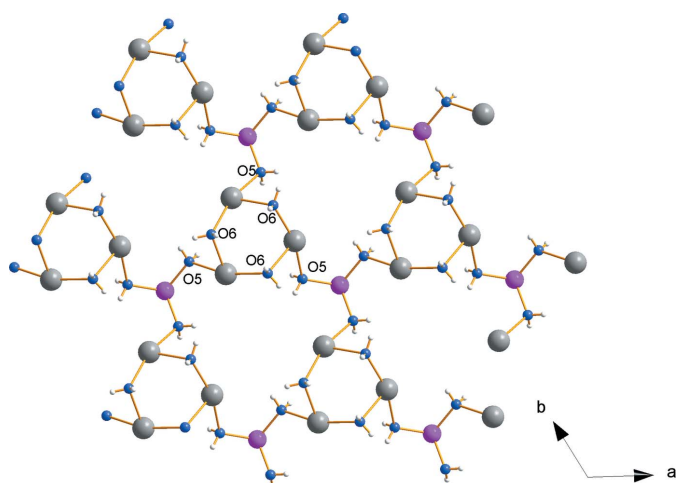


Figure 5
Cation–water coordination network within the *ab* plane. Sodium = gray, oxygen = blue, lithium = pink, hydrogen = white.

The lithium cation is coordinated by three water molecules (O5) and the apex (O3) of a sulfate anion containing S1 completes a tetrahedron (Fig. 2). Thus, the trimeric $\text{Na}_3(\text{H}_2\text{O})_3$ and the double tetrahedron $\text{Li}(\text{H}_2\text{O})_3(\text{SO}_4)$ form the characteristic structural units of this compound. In Fig. 4, the arrangement of these units is shown within the unit cell separately for $\text{Na}_3(\text{H}_2\text{O})_3$ (Fig. 4*a*) and $\text{Li}(\text{H}_2\text{O})_3(\text{SO}_4)$ (Fig. 4*b*). In Fig. 4*b* the sulfate anions with S2 are added as darker colored tetrahedra. The repeat unit requires stacking of six such units along the *c*-axis direction. The uniform orientation of the units underlines the polar character of the *c* axis.

3. Supramolecular features

The overall structure of the compound is polymeric with water and sulfate anions connecting the cations. The three water molecules coordinated at the lithium cation are at the same time coordinated to three sodium cations, each sodium ion belonging to another trimeric sodium ring forming a water–cation coordination network, as shown in Fig. 5. When including the entire coordination spheres of sodium, one can

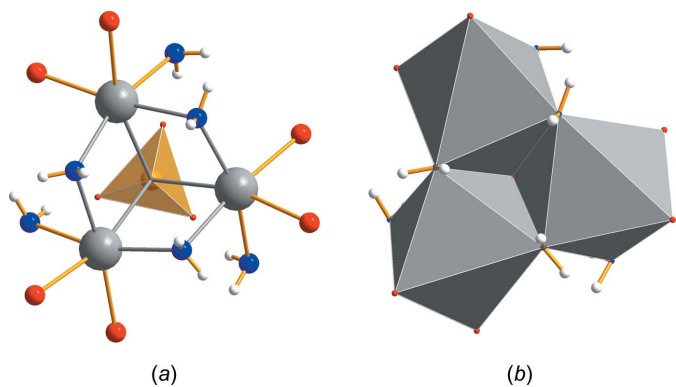


Figure 6
Representation of the sodium ion coordination within a trimeric unit: (a) stick and ball, (b) polyhedrons.

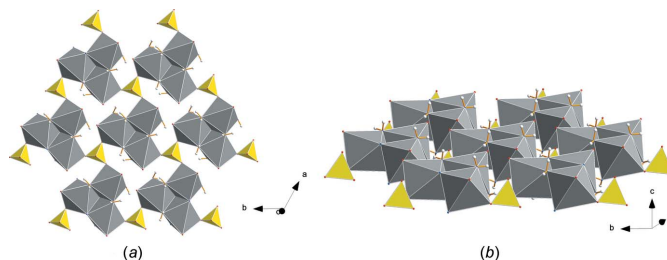


Figure 7
Interconnection of trimeric units within one layer by sulfate tetrahedra with the S1 sulfur atom viewed from two directions (*a* and *b*).

describe the trimers as edge-bridged octahedra, as illustrated in Fig. 6*a* and 6*b*. Thereby, the O4 oxygen from the sulfate anion of S2 represents a common coordination point from below (Fig. 6*a*). The height of sulfur S1 along the *c* axis is near that of Na1. Thus, the three corners of this sulfate tetrahedron connect three trimeric units within a sodium ion layer, as shown in Fig. 7 from two viewing angles. As shown in Fig. 6, the sulfate with S2 is positioned with its oxygen atom (O4) at the center below the trimeric units, and thus the other three O1 atoms of this sulfate anion connect three trimeric sodium units from the adjacent layer below (Fig. 8). In this way, the sulfate with S2 acts as a connector between sodium layers and the sulfate with S1 within one layer. Additional interconnections between layers are realized by the sulfate of S1 as

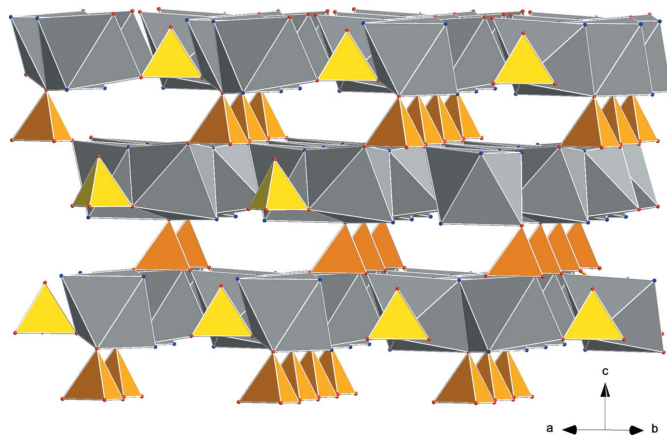


Figure 8
Interconnections of sodium layers by sulfate tetrahedra with the S2 sulfur atom (dark yellow).

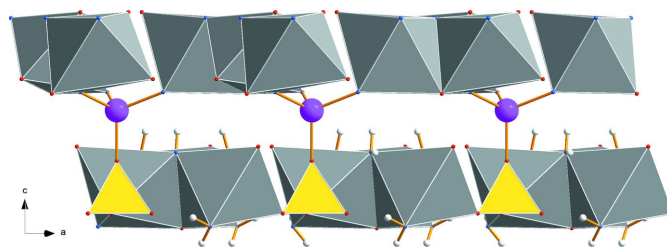


Figure 9
Interconnections of sodium layers by sulfate tetrahedra with the S2 sulfur atom (dark yellow).

Table 1
Hydrogen-bond geometry (Å, °) at 273 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O6-H6A\cdots O2^i$	0.77 (5)	2.00 (5)	2.764 (11)	170 (5)
$O6-H6B\cdots O1$	0.83 (4)	2.15 (4)	2.937 (7)	157 (4)
$O5-H5B\cdots O1^{ii}$	0.79 (4)	1.92 (4)	2.694 (7)	165 (4)
$O5-H5A\cdots O2^{iii}$	0.89 (4)	1.97 (4)	2.828 (6)	163 (3)

Symmetry codes: (i) $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$; (ii) $x - \frac{1}{3}, x - y + \frac{1}{3}, z - \frac{1}{6}$; (iii) $-x + y, -x + 1, z$.

part of the double tetrahedron $Li(H_2O)_3(SO_4)$, as illustrated in Fig. 9.

Investigation of the hydrogen-bond network (Table 1) revealed that, interestingly, the water molecules form hydrogen bonds only to the sulfate groups, but not between themselves as is observed in a channel-like arrangement in $Li_2SO_4 \cdot H_2O$ (Fig. 10). However, as can be seen from Fig. 11, the hydrogen atoms H1 and H3 share O1 as a common acceptor atom of the sulfate with S1, and H2 and H4 do the same with O2 at the sulfate anion of S2. The bond lengths vary between 1.92 and 2.15 Å. Fig. 12 shows a larger part of the

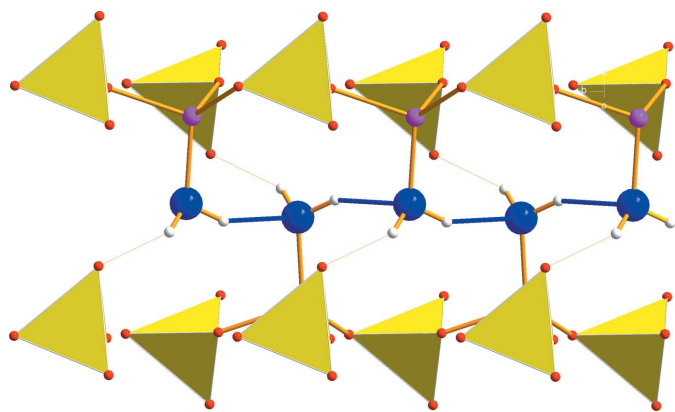


Figure 10
Hydrogen-bonded (blue bonds) chain of water molecules along the b -axis direction in the structure of $Li_2SO_4 \cdot H_2O$ (Fugel *et al.*, 2019)

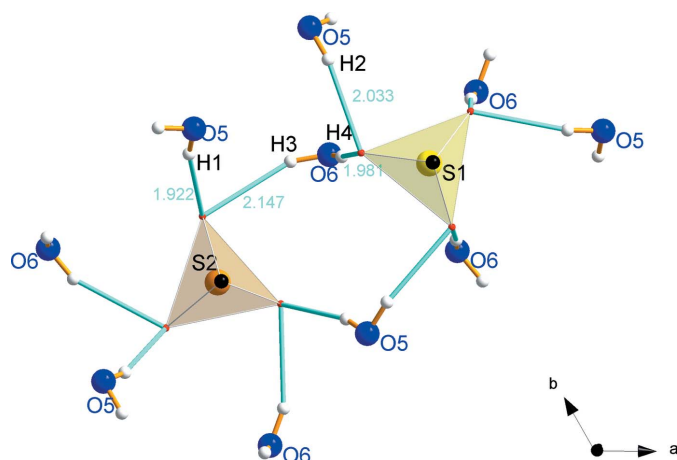


Figure 11
Hydrogen bonds from water molecules to the S1 and S2 sulfate groups.

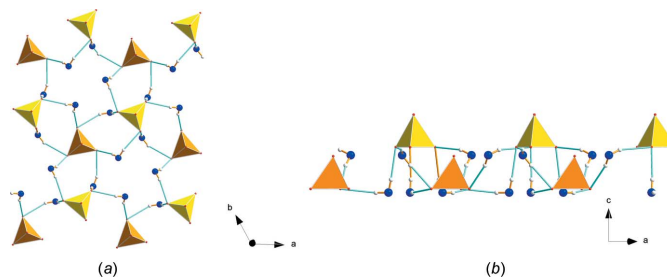


Figure 12
Larger part of the hydrogen-bond network projected on (a) the ab plane and (b) the ac plane.

hydrogen-bond network, projected both along the c axis (Fig. 12a) and perpendicular to the c axis (Fig. 12b). From the latter, it can be recognized that the hydrogen bonds contribute to the bonding strength within a layer, but not between the layers. Connections between the layers are established by cation–anion coordination as shown in Figs. 8 and 9.

4. Database survey

In the Inorganic Crystal Structure Database (ICSD), only 1164 records with space group $R3c$ (No. 161) can be found. Most of them belong to the $LiNbO_3$ or Whitlockite type [Whitlockite = $MgCa_9(PO_4)_6(HPO_4)$]. Compounds containing lithium in this space group numbered 179, of which 148 belong again to $LiNbO_3$ type. The isomorphous molybdate (ICSD col 65006, col 420160) represents a structure type of its own. The isomorphous selenate $LiNa_3(SeO_4)_2 \cdot 6H_2O$ (Kaminskii *et al.* 2007) could not be found in the ICSD. Interestingly, the mineral chlorartinite, $Mg_2[Cl(OH)CO_3] \cdot 2H_2O$, which forms easily in MgO-based building materials, also crystallizes in the space group $R3c$ (Sugimoto *et al.*, 2006).

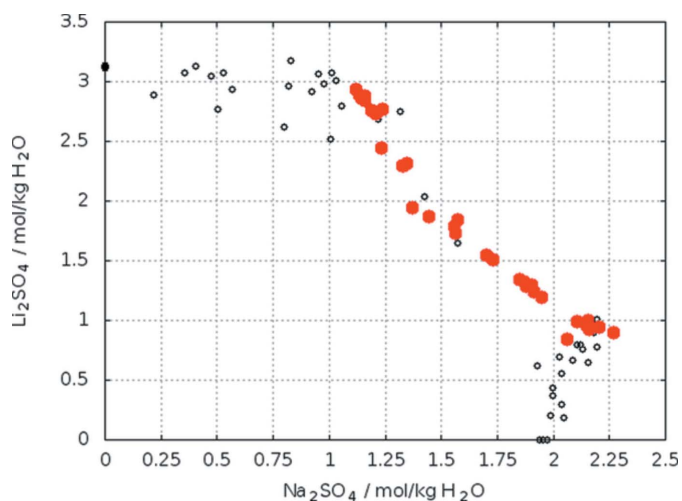


Figure 13
Solubility data in the system $Li_2SO_4-Na_2SO_4-H_2O$ at 298 K (Sohr *et al.*, 2017). Crystallization points of $LiNa_3(SO_4)_2 \cdot 6H_2O$ are shown in red.

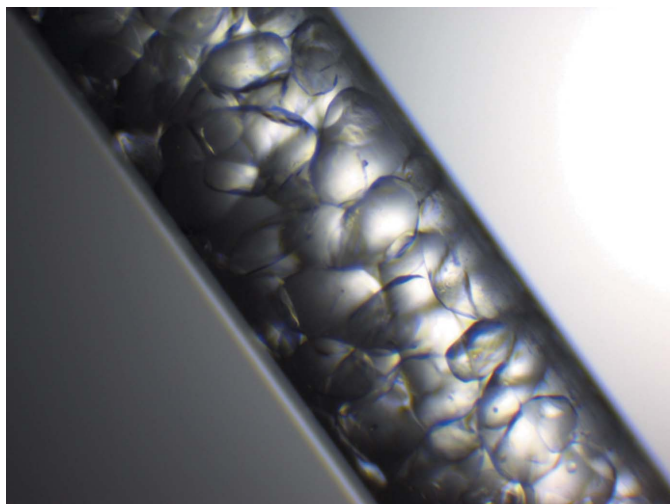


Figure 14
Image of a Hilgenberg capillary (diameter 0.5 mm) filled with crystals of $\text{LiNa}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ by means of centrifugal compaction.

5. Synthesis, crystallization and characterization

Single crystals were grown from about 120 mL of an aqueous solution containing Li_2SO_4 and Na_2SO_4 in a molar ratio of approx. 1:1 and an absolute concentration well below the solubility line (Fig. 13). The solution was kept in a desiccator with 50% H_2SO_4 solution as drying agent. Over two weeks, a number of crystals with sizes of 1–7 mm were formed that showed the typical trigonal–pyramidal form. Small pieces were cut for XRD measurements. The density of 1.995 g cm^{-3} calculated from the parameters at 293 K (Table 1) is in excellent agreement with the experimental value of 2.009 g cm^{-3} as cited in Groth (1908).

Attempts were made to record powder XRD patterns from quickly ground crystals. Large crystals appear stable at least for some minutes on a filter paper. However, when grinding to achieve a crystal powder, dehydration took place. In cases of less intensive grinding, the texture effects were too large for a representative powder XRD pattern. Thus, particularly for powder XRD measurements, a suspension of fine crystals was

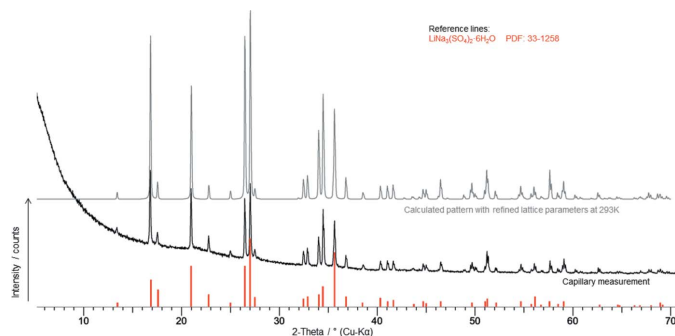


Figure 15
Powder XRD pattern of $\text{LiNa}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ recorded from a rotating capillary. Scan rate: 20 sec, steps 0.023° . For comparison, the calculated powder pattern from structural data at 293 K is also shown.

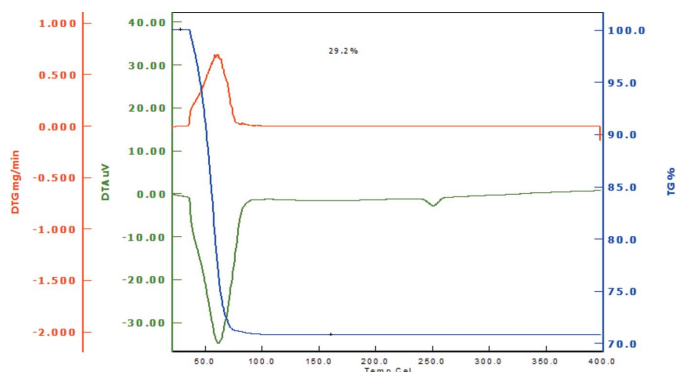


Figure 16
Thermal analysis of $\text{LiNa}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Heating rate: 5 K min^{-1} ; N_2 purge: 300 ml min^{-1} .

prepared: To a 2 molar solution of Na_2SO_4 , an equivalent amount of anhydrous Li_2SO_4 was added. The suspension was stirred two days at 298 K. The supernatant solution was decanted and subsequently some slurry was transferred into the expanded, upper part of a Hilgenberg glass capillary. By means of a centrifuge (30 minutes at 4000 r.p.m.), the crystals were pressed into the capillary. This way the available capillary volume was effectively filled with crystals (Fig. 14). A PXRD pattern obtained under rotation is shown in Fig. 15 in comparison with the one calculated from the crystal structure.

The powder pattern was measured at room temperature on a Bruker D8 Discover diffractometer in Bragg–Brentano geometry with $\text{Cu } K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a linear detector Văntec-1 (geometry angle 1°). The measurements were made with a Göbel mirror as monochromator with a 1.0 mm slit and a 2.5° primary soller. The generator was set to 40 kV/40 mA. The program *TOPAS 5.0* (Bruker, 2009) was used to refine the lattice parameters (Fig. 1). The solved structure from single crystal XRD at 293K was used as starting point of the refinement.

Thermal analyses (Fig. 16) were performed from roughly crushed, large single crystals. Water is released in one step below 353 K. The mass loss of 29.2% is near the theoretical value of 28.7%. In a second experiment, the measured value was 29.1%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Structure solution using direct methods and a refinement of the atomic positions with respect to the isotropic displacement parameters led to the positions of the Na, Li, S and O atoms. The positions of the H atoms could be located from residual electron-density maxima after further refinement. H atoms were refined isotropically.

Acknowledgements

Thanks to Regina Mossig for recording the thermal analyses.

Table 2
Experimental details.

	90 K	180 K	260 K	273 K	293 K
Crystal data					
Chemical formula	LiNa ₃ (SO ₄) ₂ ·6H ₂ O	LiNa ₃ (SO ₄) ₂ ·6H ₂ O	LiNa ₃ (SO ₄) ₂ ·6H ₂ O	LiNa ₃ (SO ₄) ₂ ·6H ₂ O	LiNa ₃ (SO ₄) ₂ ·6H ₂ O
<i>M_r</i>	376.13	376.13	376.13	376.13	376.13
Crystal system, space group	Trigonal, <i>R3c:H</i>	Trigonal, <i>R3c:H</i>	Trigonal, <i>R3c:H</i>	Trigonal, <i>R3c:H</i>	Trigonal, <i>R3c:H</i>
<i>a</i> , <i>c</i> (Å)	8.3876 (13), 30.048 (7)	8.4006 (19), 30.111 (9)	8.426 (2), 30.197 (4)	8.4337 (17), 30.235 (6)	8.457 (7), 30.33 (3)
<i>V</i> (Å ³)	1830.7 (7)	1840.3 (10)	1856.6 (10)	1862.4 (8)	1879 (4)
<i>Z</i>	6	6	6	6	6
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.62	0.61	0.61	0.61	0.60
Crystal size (mm)	0.3 × 0.15 × 0.1	0.3 × 0.15 × 0.1	0.3 × 0.15 × 0.1	0.3 × 0.15 × 0.1	0.3 × 0.15 × 0.1
Data collection					
Diffractometer	Stoe IPDS 2	Stoe IPDS 2	Stoe IPDS 2	Stoe IPDS 2	Stoe IPDS 2T
Absorption correction	Integration Coppens (1970)	Integration Coppens (1970)	Integration Coppens (1970)	Integration Coppens (1970)	Integration Coppens (1970)
<i>T_{min}</i> , <i>T_{max}</i>	0.924, 0.945	0.682, 0.941	0.864, 0.938	0.773, 0.866	0.517, 0.844
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	12154, 1089, 1089	4345, 1088, 1087	5068, 915, 906	8584, 1159, 1141	1376, 730, 695
<i>R_{int}</i>	0.027	0.035	0.034	0.035	0.054
(sin θ/λ) _{max} (Å ⁻¹)	0.685	0.692	0.643	0.694	0.641
Refinement					
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.013, 0.036, 1.14	0.021, 0.053, 1.18	0.017, 0.043, 1.13	0.019, 0.053, 1.28	0.038, 0.105, 1.11
No. of reflections	1089	1088	915	1159	730
No. of parameters	78	78	78	77	78
No. of restraints	5	1	1	1	5
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.16, -0.18	0.23, -0.33	0.14, -0.20	0.19, -0.33	0.33, -0.47
Absolute structure	Flack <i>x</i> determined using 539 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Classical Flack method preferred over Parsons because s.u. lower	Flack <i>x</i> determined using 437 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 551 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter	0.01 (3)	-0.08 (10)	-0.04 (6)	0.04 (4)	-0.3 (3)

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2017) and *publCIF* (Westrip, 2010).

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supporting information

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LiNa₃(SO₄)₂·6H₂O: a lithium double salt causing trouble in the industrial conversion of Li₂SO₄ into LiOH

Horst Schmidt, Iris Paschke and Wolfgang Voigt

Computing details

For all structures, data collection: *X-AREA* (Stoe & Cie, 2015); cell refinement: *X-AREA* (Stoe & Cie, 2015); data reduction: *X-RED* (Stoe & Cie, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2017); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Lithium trisodium bis(sulfate) hexahydrate (Na₃_Li_2SO₄_6H₂O-90K)

Crystal data

LiNa₃(SO₄)₂·6H₂O
 $M_r = 376.13$
 Trigonal, *R3c:H*
 $a = 8.3876$ (13) Å
 $c = 30.048$ (7) Å
 $V = 1830.7$ (7) Å³
 $Z = 6$
 $F(000) = 1152$

$D_x = 2.047$ Mg m⁻³
 Mo *K*α radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2749 reflections
 $\theta = 25.0$ – 27.5°
 $\mu = 0.62$ mm⁻¹
 $T = 90$ K
 Needle, colourless
 $0.3 \times 0.15 \times 0.1$ mm

Data collection

Stoe IPDS 2
 diffractometer
 Radiation source: sealed X-ray tube, 12 x 0.4
 mm long-fine focus
 Plane graphite monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 Absorption correction: integration
 Coppens (1970)

$T_{\min} = 0.924$, $T_{\max} = 0.945$
 12154 measured reflections
 1089 independent reflections
 1089 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 3.1^\circ$
 $h = -10 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -40 \rightarrow 40$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.013$
 $wR(F^2) = 0.036$
 $S = 1.14$
 1089 reflections
 78 parameters
 5 restraints
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 0.6042P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.16$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³
 Extinction correction: SHELXL2018/3
 (Sheldrick 2015),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0037 (7)

Absolute structure: Flack x determined using
539 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.01 (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	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.666667	0.333333	0.15432 (13)	0.0085 (7)
Na1	0.23426 (7)	0.26504 (7)	0.06063 (2)	0.00705 (14)
S1	0.666667	0.333333	0.04323 (2)	0.00332 (12)
S2	0.333333	0.666667	0.12552 (2)	0.00325 (12)
O1	0.39254 (13)	0.53800 (12)	0.10892 (3)	0.00609 (18)
O2	0.51766 (12)	0.36335 (12)	0.02615 (3)	0.00667 (18)
O3	0.666667	0.333333	0.09154 (6)	0.0095 (4)
O4	0.333333	0.666667	0.17470 (6)	0.0067 (3)
O5	0.14513 (13)	0.42897 (12)	0.01016 (3)	0.00656 (17)
H5A	0.053 (2)	0.429 (3)	0.0194 (7)	0.016 (5)*
H5B	0.106 (3)	0.363 (3)	-0.0120 (6)	0.020 (5)*
O6	-0.02932 (13)	0.20979 (13)	0.10180 (3)	0.00744 (19)
H6B	-0.007 (3)	0.316 (2)	0.1019 (8)	0.017 (5)*
H6A	-0.022 (3)	0.190 (3)	0.1279 (5)	0.017 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.0089 (10)	0.0089 (10)	0.0078 (16)	0.0044 (5)	0.000	0.000
Na1	0.0065 (2)	0.0076 (2)	0.0072 (2)	0.00369 (19)	0.00175 (17)	0.00177 (18)
S1	0.00352 (15)	0.00352 (15)	0.0029 (2)	0.00176 (8)	0.000	0.000
S2	0.00334 (15)	0.00334 (15)	0.0031 (2)	0.00167 (8)	0.000	0.000
O1	0.0066 (4)	0.0060 (4)	0.0074 (4)	0.0045 (3)	-0.0002 (3)	-0.0015 (3)
O2	0.0057 (4)	0.0084 (4)	0.0079 (4)	0.0050 (3)	-0.0001 (3)	0.0013 (3)
O3	0.0129 (5)	0.0129 (5)	0.0028 (8)	0.0065 (3)	0.000	0.000
O4	0.0085 (5)	0.0085 (5)	0.0031 (7)	0.0042 (2)	0.000	0.000
O5	0.0063 (4)	0.0067 (4)	0.0068 (4)	0.0034 (3)	0.0010 (3)	-0.0010 (3)
O6	0.0089 (4)	0.0068 (4)	0.0064 (4)	0.0038 (4)	0.0000 (3)	0.0003 (3)

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

Li1—O3	1.886 (4)	Na1—O4 ^v	2.6330 (14)
Li1—O5 ⁱ	1.9434 (17)	Na1—Na1 ^{vi}	3.6475 (10)
Li1—O5 ⁱⁱ	1.9435 (17)	Na1—Na1 ^{iv}	3.6475 (10)
Li1—O5 ⁱⁱⁱ	1.9435 (17)	S1—O3	1.4515 (17)

Li1—Na1 ⁱ	3.748 (2)	S1—O2 ^{vii}	1.4844 (9)
Li1—Na1 ⁱⁱⁱ	3.748 (2)	S1—O2	1.4844 (9)
Li1—Na1 ⁱⁱ	3.748 (2)	S1—O2 ^{viii}	1.4844 (9)
Na1—O2	2.3331 (10)	S2—O4	1.4777 (17)
Na1—O6 ^{iv}	2.3498 (11)	S2—O1 ^{ix}	1.4818 (9)
Na1—O6	2.3682 (11)	S2—O1	1.4818 (9)
Na1—O5	2.4036 (11)	S2—O1 ^x	1.4818 (9)
Na1—O1	2.4638 (10)		
O3—Li1—O5 ⁱ	110.37 (11)	O1—Na1—Na1 ^{vi}	122.28 (3)
O3—Li1—O5 ⁱⁱ	110.36 (11)	O4 ^v —Na1—Na1 ^{vi}	46.16 (3)
O5 ⁱ —Li1—O5 ⁱⁱ	108.56 (12)	O2—Na1—Na1 ^{iv}	102.41 (3)
O3—Li1—O5 ⁱⁱⁱ	110.36 (11)	O6 ^{iv} —Na1—Na1 ^{iv}	39.55 (3)
O5 ⁱ —Li1—O5 ⁱⁱⁱ	108.56 (12)	O6—Na1—Na1 ^{iv}	85.42 (3)
O5 ⁱⁱ —Li1—O5 ⁱⁱⁱ	108.56 (12)	O5—Na1—Na1 ^{iv}	123.78 (3)
O3—Li1—Na1 ⁱ	125.81 (5)	O1—Na1—Na1 ^{iv}	142.40 (2)
O5 ⁱ —Li1—Na1 ⁱ	34.21 (6)	O4 ^v —Na1—Na1 ^{iv}	46.16 (3)
O5 ⁱⁱ —Li1—Na1 ⁱ	74.41 (8)	Na1 ^{vi} —Na1—Na1 ^{iv}	60.0
O5 ⁱⁱⁱ —Li1—Na1 ⁱ	119.02 (15)	O2—Na1—Li1 ^{xi}	72.17 (3)
O3—Li1—Na1 ⁱⁱⁱ	125.81 (5)	O6 ^{iv} —Na1—Li1 ^{xi}	167.14 (3)
O5 ⁱ —Li1—Na1 ⁱⁱⁱ	74.40 (8)	O6—Na1—Li1 ^{xi}	104.31 (4)
O5 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	119.01 (15)	O5—Na1—Li1 ^{xi}	27.04 (3)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱⁱ	34.21 (6)	O1—Na1—Li1 ^{xi}	74.64 (5)
Na1 ⁱ —Li1—Na1 ⁱⁱⁱ	89.23 (7)	O4 ^v —Na1—Li1 ^{xi}	98.29 (5)
O3—Li1—Na1 ⁱⁱ	125.81 (5)	Na1 ^{vi} —Na1—Li1 ^{xi}	105.94 (2)
O5 ⁱ —Li1—Na1 ⁱⁱ	119.02 (15)	Na1 ^{iv} —Na1—Li1 ^{xi}	142.95 (5)
O5 ⁱⁱ —Li1—Na1 ⁱⁱ	34.21 (6)	O3—S1—O2 ^{vii}	110.23 (4)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	74.40 (8)	O3—S1—O2	110.23 (4)
Na1 ⁱ —Li1—Na1 ⁱⁱ	89.23 (7)	O2 ^{vii} —S1—O2	108.71 (5)
Na1 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	89.23 (7)	O3—S1—O2 ^{viii}	110.23 (4)
O2—Na1—O6 ^{iv}	95.05 (4)	O2 ^{vii} —S1—O2 ^{viii}	108.70 (5)
O2—Na1—O6	170.96 (4)	O2—S1—O2 ^{viii}	108.71 (5)
O6 ^{iv} —Na1—O6	88.14 (5)	O4—S2—O1 ^{ix}	109.66 (4)
O2—Na1—O5	94.07 (4)	O4—S2—O1	109.66 (4)
O6 ^{iv} —Na1—O5	162.69 (4)	O1 ^{ix} —S2—O1	109.28 (4)
O6—Na1—O5	85.10 (4)	O4—S2—O1 ^x	109.66 (4)
O2—Na1—O1	87.29 (4)	O1 ^{ix} —S2—O1 ^x	109.28 (4)
O6 ^{iv} —Na1—O1	104.11 (4)	O1—S2—O1 ^x	109.28 (4)
O6—Na1—O1	83.73 (3)	S2—O1—Na1	130.83 (5)
O5—Na1—O1	90.99 (3)	S1—O2—Na1	125.59 (6)
O2—Na1—O4 ^v	103.31 (4)	S1—O3—Li1	180.0
O6 ^{iv} —Na1—O4 ^v	85.71 (4)	S2—O4—Na1 ^{xii}	126.89 (4)
O6—Na1—O4 ^v	85.34 (4)	S2—O4—Na1 ^{xiii}	126.89 (4)
O5—Na1—O4 ^v	77.88 (4)	Na1 ^{xii} —O4—Na1 ^{xiii}	87.68 (5)
O1—Na1—O4 ^v	165.02 (3)	S2—O4—Na1 ⁱ	126.89 (4)
O2—Na1—Na1 ^{vi}	149.40 (3)	Na1 ^{xii} —O4—Na1 ⁱ	87.68 (5)
O6 ^{iv} —Na1—Na1 ^{vi}	85.68 (3)	Na1 ^{xiii} —O4—Na1 ⁱ	87.68 (5)

O6—Na1—Na1 ^{vi}	39.18 (3)	Li1 ^{xi} —O5—Na1	118.75 (8)
O5—Na1—Na1 ^{vi}	79.01 (3)	Na1 ^{vi} —O6—Na1	101.27 (4)

Symmetry codes: (i) $x+1/3, x-y+2/3, z+1/6$; (ii) $-y+4/3, -x+2/3, z+1/6$; (iii) $-x+y+1/3, y-1/3, z+1/6$; (iv) $-x+y, -x, z$; (v) $-y+2/3, -x+1/3, z-1/6$; (vi) $-y, x-y, z$; (vii) $-x+y+1, -x+1, z$; (viii) $-y+1, x-y, z$; (ix) $-y+1, x-y+1, z$; (x) $-x+y, -x+1, z$; (xi) $-y+2/3, -x+4/3, z-1/6$; (xii) $-x+y+1/3, y+2/3, z+1/6$; (xiii) $-y+1/3, -x+2/3, z+1/6$.

Sodium-Lithium-Sulfate-Hexahydrate (Na₃Li₂SO₄·6H₂O-180K)

Crystal data

3(Na)Li₂(SO₄)₆(H₂O)

$M_r = 376.13$

Trigonal, $R3c:H$

$a = 8.4006$ (19) Å

$c = 30.111$ (9) Å

$V = 1840.3$ (10) Å³

$Z = 6$

$F(000) = 1152$

$D_x = 2.036$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7724 reflections

$\theta = 2.8$ – 30.0°

$\mu = 0.61$ mm⁻¹

$T = 180$ K

Needle, colourless

$0.3 \times 0.15 \times 0.1$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration

Coppens (1970)

$T_{\min} = 0.682, T_{\max} = 0.941$

4345 measured reflections

1088 independent reflections

1087 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 29.5^\circ, \theta_{\min} = 3.1^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -40 \rightarrow 40$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.053$

$S = 1.18$

1088 reflections

78 parameters

1 restraint

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$

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

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

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ e Å⁻³

Extinction correction: SHELXL2018/3

(Sheldrick 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.055 (4)

Absolute structure: Classical Flack method

preferred over Parsons because s.u. lower

Absolute structure parameter: -0.08 (10)

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.666667	0.333333	0.15397 (15)	0.0112 (7)
Na1	0.23455 (8)	0.26585 (8)	0.06065 (3)	0.0123 (2)

S1	0.666667	0.333333	0.04314 (2)	0.00567 (18)
S2	0.333333	0.666667	0.12563 (2)	0.00580 (18)
O1	0.39232 (16)	0.53835 (14)	0.10903 (4)	0.0101 (2)
O2	0.51801 (14)	0.36299 (14)	0.02615 (4)	0.0116 (2)
O3	0.666667	0.333333	0.09124 (10)	0.0182 (6)
O4	0.333333	0.666667	0.17460 (9)	0.0113 (5)
O5	0.14543 (15)	0.42931 (14)	0.00995 (4)	0.0107 (2)
H5A	0.057 (4)	0.431 (3)	0.0205 (10)	0.019 (6)*
H5B	0.106 (4)	0.359 (4)	-0.0106 (11)	0.021 (5)*
O6	-0.02970 (15)	0.20921 (15)	0.10179 (4)	0.0125 (2)
H6B	-0.011 (4)	0.311 (5)	0.1015 (12)	0.029 (8)*
H6A	-0.023 (4)	0.189 (4)	0.1275 (11)	0.019 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.0125 (11)	0.0125 (11)	0.0087 (17)	0.0062 (5)	0.000	0.000
Na1	0.0118 (3)	0.0139 (3)	0.0119 (3)	0.0068 (2)	0.00347 (19)	0.00357 (19)
S1	0.0068 (2)	0.0068 (2)	0.0033 (3)	0.00342 (11)	0.000	0.000
S2	0.0064 (2)	0.0064 (2)	0.0046 (3)	0.00320 (11)	0.000	0.000
O1	0.0119 (4)	0.0099 (4)	0.0107 (5)	0.0073 (3)	-0.0002 (3)	-0.0020 (3)
O2	0.0095 (4)	0.0153 (5)	0.0131 (4)	0.0085 (4)	0.0002 (3)	0.0022 (3)
O3	0.0253 (9)	0.0253 (9)	0.0039 (11)	0.0127 (4)	0.000	0.000
O4	0.0143 (7)	0.0143 (7)	0.0054 (11)	0.0071 (4)	0.000	0.000
O5	0.0117 (4)	0.0099 (4)	0.0103 (5)	0.0051 (3)	0.0010 (4)	-0.0011 (3)
O6	0.0150 (5)	0.0122 (5)	0.0096 (5)	0.0064 (4)	0.0007 (3)	0.0000 (4)

Geometric parameters (Å, °)

Li1—O3	1.889 (6)	Na1—O4 ^v	2.644 (2)
Li1—O5 ⁱ	1.9454 (19)	Na1—Na1 ^{iv}	3.6617 (13)
Li1—O5 ⁱⁱ	1.9455 (19)	Na1—Na1 ^{vi}	3.6618 (13)
Li1—O5 ⁱⁱⁱ	1.9455 (19)	S1—O3	1.448 (3)
Li1—Na1 ⁱⁱ	3.756 (3)	S1—O2	1.4813 (11)
Li1—Na1 ⁱⁱⁱ	3.756 (3)	S1—O2 ^{vii}	1.4814 (11)
Li1—Na1 ⁱ	3.756 (3)	S1—O2 ^{viii}	1.4814 (11)
Na1—O2	2.3393 (12)	S2—O4	1.474 (3)
Na1—O6 ^{iv}	2.3546 (13)	S2—O1	1.4804 (11)
Na1—O6	2.3734 (13)	S2—O1 ^{ix}	1.4804 (11)
Na1—O5	2.4093 (13)	S2—O1 ^x	1.4804 (11)
Na1—O1	2.4669 (12)		
O3—Li1—O5 ⁱ	110.52 (13)	O1—Na1—Na1 ^{iv}	142.29 (3)
O3—Li1—O5 ⁱⁱ	110.52 (13)	O4 ^v —Na1—Na1 ^{iv}	46.17 (4)
O5 ⁱ —Li1—O5 ⁱⁱ	108.41 (13)	O2—Na1—Na1 ^{vi}	149.23 (3)
O3—Li1—O5 ⁱⁱⁱ	110.52 (13)	O6 ^{iv} —Na1—Na1 ^{vi}	85.51 (3)
O5 ⁱ —Li1—O5 ⁱⁱⁱ	108.41 (13)	O6—Na1—Na1 ^{vi}	39.06 (3)
O5 ⁱⁱ —Li1—O5 ⁱⁱⁱ	108.40 (13)	O5—Na1—Na1 ^{vi}	79.08 (3)

O3—Li1—Na1 ⁱⁱ	126.01 (6)	O1—Na1—Na1 ^{vi}	122.25 (3)
O5 ⁱ —Li1—Na1 ⁱⁱ	118.70 (17)	O4 ^v —Na1—Na1 ^{vi}	46.17 (4)
O5 ⁱⁱ —Li1—Na1 ⁱⁱ	34.19 (6)	Na1 ^{iv} —Na1—Na1 ^{vi}	60.0
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	74.26 (9)	O2—Na1—Li1 ^{xi}	72.31 (3)
O3—Li1—Na1 ⁱⁱⁱ	126.01 (6)	O6 ^{iv} —Na1—Li1 ^{xi}	167.18 (4)
O5 ⁱ —Li1—Na1 ⁱⁱⁱ	74.26 (9)	O6—Na1—Li1 ^{xi}	104.59 (4)
O5 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	118.70 (17)	O5—Na1—Li1 ^{xi}	26.99 (3)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱⁱ	34.19 (6)	O1—Na1—Li1 ^{xi}	74.93 (6)
Na1 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	88.94 (8)	O4 ^v —Na1—Li1 ^{xi}	98.14 (7)
O3—Li1—Na1 ⁱ	126.01 (6)	Na1 ^{iv} —Na1—Li1 ^{xi}	142.78 (5)
O5 ⁱ —Li1—Na1 ⁱ	34.19 (6)	Na1 ^{vi} —Na1—Li1 ^{xi}	105.95 (2)
O5 ⁱⁱ —Li1—Na1 ⁱ	74.27 (9)	O3—S1—O2	110.20 (6)
O5 ⁱⁱⁱ —Li1—Na1 ⁱ	118.70 (17)	O3—S1—O2 ^{vii}	110.21 (6)
Na1 ⁱⁱ —Li1—Na1 ⁱ	88.94 (8)	O2—S1—O2 ^{vii}	108.73 (6)
Na1 ⁱⁱⁱ —Li1—Na1 ⁱ	88.94 (8)	O3—S1—O2 ^{viii}	110.21 (6)
O2—Na1—O6 ^{iv}	94.92 (4)	O2—S1—O2 ^{viii}	108.73 (6)
O2—Na1—O6	171.37 (5)	O2 ^{vii} —S1—O2 ^{viii}	108.73 (6)
O6 ^{iv} —Na1—O6	87.90 (6)	O4—S2—O1	109.74 (6)
O2—Na1—O5	94.13 (4)	O4—S2—O1 ^{ix}	109.74 (6)
O6 ^{iv} —Na1—O5	162.50 (5)	O1—S2—O1 ^{ix}	109.20 (6)
O6—Na1—O5	85.35 (5)	O4—S2—O1 ^x	109.74 (6)
O2—Na1—O1	87.57 (4)	O1—S2—O1 ^x	109.20 (6)
O6 ^{iv} —Na1—O1	104.10 (4)	O1 ^{ix} —S2—O1 ^x	109.20 (6)
O6—Na1—O1	83.82 (4)	S2—O1—Na1	130.92 (7)
O5—Na1—O1	91.21 (4)	S1—O2—Na1	125.78 (7)
O2—Na1—O4 ^v	103.11 (6)	S1—O3—Li1	180.0
O6 ^{iv} —Na1—O4 ^v	85.59 (5)	S2—O4—Na1 ^{xii}	126.90 (6)
O6—Na1—O4 ^v	85.22 (5)	S2—O4—Na1 ^{xiii}	126.90 (6)
O5—Na1—O4 ^v	77.78 (5)	Na1 ^{xii} —O4—Na1 ^{xiii}	87.67 (9)
O1—Na1—O4 ^v	165.06 (3)	S2—O4—Na1 ⁱ	126.90 (6)
O2—Na1—Na1 ^{iv}	102.10 (4)	Na1 ^{xii} —O4—Na1 ⁱ	87.67 (9)
O6 ^{iv} —Na1—Na1 ^{iv}	39.43 (3)	Na1 ^{xiii} —O4—Na1 ⁱ	87.67 (9)
O6—Na1—Na1 ^{iv}	85.26 (3)	Li1 ^{xi} —O5—Na1	118.83 (9)
O5—Na1—Na1 ^{iv}	123.70 (3)	Na1 ^{vi} —O6—Na1	101.51 (5)

Symmetry codes: (i) $x+1/3, x-y+2/3, z+1/6$; (ii) $-y+4/3, -x+2/3, z+1/6$; (iii) $-x+y+1/3, y-1/3, z+1/6$; (iv) $-x+y, -x, z$; (v) $-y+2/3, -x+1/3, z-1/6$; (vi) $-y, x-y, z$; (vii) $-y+1, x-y, z$; (viii) $-x+y+1, -x+1, z$; (ix) $-x+y, -x+1, z$; (x) $-y+1, x-y+1, z$; (xi) $-y+2/3, -x+4/3, z-1/6$; (xii) $-x+y+1/3, y+2/3, z+1/6$; (xiii) $-y+1/3, -x+2/3, z+1/6$.

Sodium-Lithium-Sulfate-Hexahydrate (Na₃Li₂SO₄·6H₂O-260K)

Crystal data

3(Na)Li₂(SO₄)₆(H₂O)

$M_r = 376.13$

Trigonal, $R3c:H$

$a = 8.426$ (2) Å

$c = 30.197$ (4) Å

$V = 1856.6$ (10) Å³

$Z = 6$

$F(000) = 1152$

$D_x = 2.018$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4304 reflections

$\theta = 2.6$ – 21.0°

$\mu = 0.61$ mm⁻¹

$T = 260$ K

Needle, colourless

$0.3 \times 0.15 \times 0.1$ mm

Data collection

Stoe IPDS 2 diffractometer	$T_{\min} = 0.864$, $T_{\max} = 0.938$
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	5068 measured reflections
Plane graphite monochromator	915 independent reflections
Detector resolution: 6.67 pixels mm ⁻¹ rotation method scans	906 reflections with $I > 2\sigma(I)$
Absorption correction: integration Coppens (1970)	$R_{\text{int}} = 0.034$
	$\theta_{\max} = 27.2^\circ$, $\theta_{\min} = 3.1^\circ$
	$h = -10 \rightarrow 10$
	$k = -9 \rightarrow 10$
	$l = -38 \rightarrow 38$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
Least-squares matrix: full	$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.017$	$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.043$	Extinction correction: SHELXL2018/3 (Sheldrick 2015),
$S = 1.13$	$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
915 reflections	Extinction coefficient: 0.0031 (4)
78 parameters	Absolute structure: Flack x determined using 437 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
1 restraint	Absolute structure parameter: -0.04 (6)
Hydrogen site location: difference Fourier map	
All H-atom parameters refined	
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.5038P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.333333	0.666667	0.8465 (2)	0.0164 (12)
Na1	0.76508 (11)	0.73321 (11)	0.93934 (4)	0.0204 (2)
S1	0.333333	0.666667	0.95693 (2)	0.01085 (19)
S2	0.666667	0.333333	0.87429 (2)	0.01117 (19)
O1	0.6085 (2)	0.46143 (19)	0.89076 (5)	0.0167 (3)
O2	0.4815 (2)	0.6374 (2)	0.97377 (5)	0.0188 (3)
O3	0.333333	0.666667	0.90900 (9)	0.0282 (7)
O4	0.666667	0.333333	0.82539 (8)	0.0181 (6)
O5	0.8541 (2)	0.56971 (19)	0.99018 (5)	0.0172 (3)
H5A	0.949 (5)	0.569 (4)	0.9803 (10)	0.027 (8)*
H5B	0.890 (4)	0.630 (4)	1.0103 (11)	0.027 (8)*
O6	1.0306 (2)	0.7917 (2)	0.89835 (6)	0.0200 (3)
H6B	1.014 (5)	0.690 (6)	0.8961 (11)	0.045 (10)*
H6A	1.017 (5)	0.807 (5)	0.8738 (12)	0.044 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.0178 (17)	0.0178 (17)	0.014 (3)	0.0089 (9)	0.000	0.000
Na1	0.0190 (4)	0.0218 (4)	0.0207 (4)	0.0104 (4)	0.0049 (3)	0.0054 (3)
S1	0.0115 (2)	0.0115 (2)	0.0096 (4)	0.00575 (12)	0.000	0.000
S2	0.0113 (2)	0.0113 (2)	0.0109 (4)	0.00565 (12)	0.000	0.000
O1	0.0181 (7)	0.0165 (7)	0.0194 (7)	0.0114 (6)	-0.0007 (5)	-0.0030 (5)
O2	0.0160 (7)	0.0236 (7)	0.0222 (7)	0.0138 (6)	0.0009 (6)	0.0032 (6)
O3	0.0384 (11)	0.0384 (11)	0.0076 (14)	0.0192 (6)	0.000	0.000
O4	0.0221 (9)	0.0221 (9)	0.0102 (12)	0.0110 (4)	0.000	0.000
O5	0.0184 (7)	0.0154 (7)	0.0171 (7)	0.0079 (6)	0.0020 (6)	-0.0013 (6)
O6	0.0223 (8)	0.0196 (8)	0.0179 (7)	0.0102 (7)	0.0005 (6)	-0.0009 (6)

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

Li1—O3	1.888 (6)	Na1—O4 ^v	2.656 (2)
Li1—O5 ⁱ	1.948 (3)	Na1—Na1 ^{iv}	3.6830 (17)
Li1—O5 ⁱⁱ	1.948 (3)	Na1—Na1 ^{vi}	3.6830 (17)
Li1—O5 ⁱⁱⁱ	1.948 (3)	S1—O3	1.447 (3)
Li1—Na1 ⁱⁱⁱ	3.770 (4)	S1—O2	1.4788 (15)
Li1—Na1 ⁱ	3.770 (4)	S1—O2 ^{vii}	1.4788 (15)
Li1—Na1 ⁱⁱ	3.770 (4)	S1—O2 ^{viii}	1.4788 (15)
Na1—O2	2.3478 (17)	S2—O4	1.477 (2)
Na1—O6 ^{iv}	2.3584 (18)	S2—O1 ^{ix}	1.4769 (14)
Na1—O6	2.3825 (19)	S2—O1 ^x	1.4769 (14)
Na1—O5	2.4188 (16)	S2—O1	1.4769 (14)
Na1—O1	2.4727 (17)		
O3—Li1—O5 ⁱ	110.85 (17)	O1—Na1—Na1 ^{iv}	142.14 (4)
O3—Li1—O5 ⁱⁱ	110.85 (17)	O4 ^v —Na1—Na1 ^{iv}	46.11 (4)
O5 ⁱ —Li1—O5 ⁱⁱ	108.06 (18)	O2—Na1—Na1 ^{vi}	149.08 (5)
O3—Li1—O5 ⁱⁱⁱ	110.85 (17)	O6 ^{iv} —Na1—Na1 ^{vi}	85.36 (5)
O5 ⁱ —Li1—O5 ⁱⁱⁱ	108.06 (18)	O6—Na1—Na1 ^{vi}	38.79 (4)
O5 ⁱⁱ —Li1—O5 ⁱⁱⁱ	108.06 (18)	O5—Na1—Na1 ^{vi}	79.18 (5)
O3—Li1—Na1 ⁱⁱⁱ	126.24 (8)	O1—Na1—Na1 ^{vi}	122.10 (5)
O5 ⁱ —Li1—Na1 ⁱⁱⁱ	118.2 (2)	O4 ^v —Na1—Na1 ^{vi}	46.11 (4)
O5 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	73.96 (12)	Na1 ^{iv} —Na1—Na1 ^{vi}	60.000 (1)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱⁱ	34.14 (9)	O2—Na1—Li1 ^{xi}	72.52 (5)
O3—Li1—Na1 ⁱ	126.24 (8)	O6 ^{iv} —Na1—Li1 ^{xi}	167.16 (6)
O5 ⁱ —Li1—Na1 ⁱ	34.14 (9)	O6—Na1—Li1 ^{xi}	104.84 (6)
O5 ⁱⁱ —Li1—Na1 ⁱ	118.2 (2)	O5—Na1—Li1 ^{xi}	26.88 (5)
O5 ⁱⁱⁱ —Li1—Na1 ⁱ	73.96 (12)	O1—Na1—Li1 ^{xi}	75.28 (8)
Na1 ⁱⁱⁱ —Li1—Na1 ⁱ	88.61 (11)	O4 ^v —Na1—Li1 ^{xi}	98.04 (8)
O3—Li1—Na1 ⁱⁱ	126.24 (8)	Na1 ^{iv} —Na1—Li1 ^{xi}	142.58 (7)
O5 ⁱ —Li1—Na1 ⁱⁱ	73.96 (12)	Na1 ^{vi} —Na1—Li1 ^{xi}	105.97 (3)
O5 ⁱⁱ —Li1—Na1 ⁱⁱ	34.14 (9)	O3—S1—O2	110.11 (7)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	118.2 (2)	O3—S1—O2 ^{vii}	110.12 (7)

Na1 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	88.61 (11)	O2—S1—O2 ^{vii}	108.82 (7)
Na1 ⁱ —Li1—Na1 ⁱⁱ	88.61 (11)	O3—S1—O2 ^{viii}	110.12 (7)
O2—Na1—O6 ^{iv}	94.66 (6)	O2—S1—O2 ^{viii}	108.82 (7)
O2—Na1—O6	171.88 (7)	O2 ^{vii} —S1—O2 ^{viii}	108.82 (7)
O6 ^{iv} —Na1—O6	87.76 (9)	O4—S2—O1 ^{ix}	109.68 (7)
O2—Na1—O5	94.30 (6)	O4—S2—O1 ^x	109.68 (7)
O6 ^{iv} —Na1—O5	162.39 (7)	O1 ^{ix} —S2—O1 ^x	109.26 (7)
O6—Na1—O5	85.48 (7)	O4—S2—O1	109.69 (6)
O2—Na1—O1	87.96 (6)	O1 ^{ix} —S2—O1	109.26 (7)
O6 ^{iv} —Na1—O1	104.13 (6)	O1 ^x —S2—O1	109.26 (7)
O6—Na1—O1	83.93 (6)	S2—O1—Na1	131.17 (9)
O5—Na1—O1	91.31 (6)	S1—O2—Na1	126.11 (9)
O2—Na1—O4 ^v	103.01 (6)	S1—O3—Li1	180.0
O6 ^{iv} —Na1—O4 ^v	85.37 (6)	S2—O4—Na1 ^{xii}	126.82 (5)
O6—Na1—O4 ^v	84.90 (6)	S2—O4—Na1 ^{xiii}	126.82 (5)
O5—Na1—O4 ^v	77.85 (6)	Na1 ^{xii} —O4—Na1 ^{xiii}	87.78 (7)
O1—Na1—O4 ^v	165.00 (5)	S2—O4—Na1 ⁱⁱⁱ	126.82 (5)
O2—Na1—Na1 ^{iv}	101.74 (5)	Na1 ^{xii} —O4—Na1 ⁱⁱⁱ	87.78 (7)
O6 ^{iv} —Na1—Na1 ^{iv}	39.26 (5)	Na1 ^{xiii} —O4—Na1 ⁱⁱⁱ	87.78 (7)
O6—Na1—Na1 ^{iv}	85.03 (4)	Li1 ^{xi} —O5—Na1	118.98 (12)
O5—Na1—Na1 ^{iv}	123.73 (5)	Na1 ^{vi} —O6—Na1	101.95 (7)

Symmetry codes: (i) $-x+y+2/3, y+1/3, z-1/6$; (ii) $-y+2/3, -x+4/3, z-1/6$; (iii) $x-1/3, x-y+1/3, z-1/6$; (iv) $-x+y+1, -x+2, z$; (v) $-y+4/3, -x+5/3, z+1/6$; (vi) $-y+2, x-y+1, z$; (vii) $-y+1, x-y+1, z$; (viii) $-x+y, -x+1, z$; (ix) $-x+y+1, -x+1, z$; (x) $-y+1, x-y, z$; (xi) $-y+4/3, -x+2/3, z+1/6$; (xii) $-x+y+2/3, y-2/3, z-1/6$; (xiii) $-y+5/3, -x+4/3, z-1/6$.

Sodium-Lithium-Sulfate-Hexahydrate (Na₃Li₂SO₄·6H₂O-273K)

Crystal data

3(Na)Li₂(SO₄)₆(H₂O)

$M_r = 376.13$

Trigonal, $R3c:H$

$a = 8.4337$ (17) Å

$c = 30.235$ (6) Å

$V = 1862.4$ (8) Å³

$Z = 6$

$F(000) = 1152$

$D_x = 2.012$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10790 reflections

$\theta = 2.8-27.5^\circ$

$\mu = 0.61$ mm⁻¹

$T = 273$ K

Needle, colourless

$0.3 \times 0.15 \times 0.1$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4

mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration

Coppens (1970)

$T_{\min} = 0.773, T_{\max} = 0.866$

8584 measured reflections

1159 independent reflections

1141 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 29.6^\circ, \theta_{\min} = 3.1^\circ$

$h = -11 \rightarrow 11$

$k = -10 \rightarrow 11$

$l = -40 \rightarrow 40$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.053$

$S = 1.28$
 1159 reflections
 77 parameters
 1 restraint
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 1.6465P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack x determined using
 551 quotients $[(I^-)-(I^+)]/[(I^-)+(I^+)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.04 (4)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.666667	0.333333	0.1535 (2)	0.0180 (12)
Na1	0.23496 (12)	0.26693 (13)	0.06069 (4)	0.0207 (2)
S1	0.666667	0.333333	0.04304 (3)	0.01061 (16)
S2	0.333333	0.666667	0.12574 (3)	0.01110 (16)
O1	0.3914 (2)	0.5385 (2)	0.10929 (5)	0.0170 (3)
O2	0.5185 (2)	0.3624 (2)	0.02624 (6)	0.0193 (3)
O3	0.666667	0.333333	0.09098 (10)	0.0290 (7)
O4	0.333333	0.666667	0.17459 (9)	0.0190 (5)
O5	0.1459 (2)	0.4305 (2)	0.00968 (6)	0.0174 (3)
H5A	0.047 (6)	0.434 (5)	0.0201 (13)	0.034 (10)*
H5B	0.108 (5)	0.365 (5)	-0.0120 (13)	0.030 (9)*
O6	-0.0306 (2)	0.2082 (2)	0.10174 (6)	0.0205 (3)
H6B	-0.009 (6)	0.314 (7)	0.1031 (13)	0.043 (11)*
H6A	-0.023 (7)	0.188 (6)	0.1279 (15)	0.051 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.0190 (18)	0.0190 (18)	0.016 (3)	0.0095 (9)	0.000	0.000
Na1	0.0189 (4)	0.0228 (5)	0.0206 (4)	0.0107 (4)	0.0053 (3)	0.0055 (4)
S1	0.0116 (2)	0.0116 (2)	0.0087 (3)	0.00578 (11)	0.000	0.000
S2	0.0112 (2)	0.0112 (2)	0.0108 (4)	0.00562 (11)	0.000	0.000
O1	0.0181 (7)	0.0173 (7)	0.0192 (7)	0.0117 (6)	-0.0011 (6)	-0.0032 (6)
O2	0.0166 (7)	0.0242 (8)	0.0224 (7)	0.0141 (6)	0.0000 (6)	0.0033 (6)
O3	0.0393 (12)	0.0393 (12)	0.0083 (13)	0.0196 (6)	0.000	0.000
O4	0.0230 (8)	0.0230 (8)	0.0110 (12)	0.0115 (4)	0.000	0.000
O5	0.0186 (7)	0.0158 (7)	0.0173 (7)	0.0083 (6)	0.0021 (6)	-0.0009 (6)
O6	0.0235 (9)	0.0193 (8)	0.0186 (8)	0.0106 (7)	0.0004 (6)	-0.0009 (7)

Geometric parameters (Å, °)

Li1—O3	1.889 (7)	Na1—O4 ^v	2.661 (2)
Li1—O5 ⁱ	1.948 (3)	Na1—Na1 ^{vi}	3.6879 (18)
Li1—O5 ⁱⁱ	1.948 (3)	Na1—Na1 ^{iv}	3.6879 (18)
Li1—O5 ⁱⁱⁱ	1.948 (3)	S1—O3	1.449 (3)
Li1—Na1 ⁱ	3.775 (4)	S1—O2 ^{vii}	1.4783 (16)
Li1—Na1 ⁱⁱⁱ	3.775 (4)	S1—O2	1.4783 (16)
Li1—Na1 ⁱⁱ	3.775 (4)	S1—O2 ^{viii}	1.4783 (16)
Na1—O2	2.3509 (19)	S2—O4	1.477 (3)
Na1—O6 ^{iv}	2.362 (2)	S2—O1 ^{ix}	1.4781 (16)
Na1—O6	2.386 (2)	S2—O1 ^x	1.4781 (16)
Na1—O5	2.4253 (18)	S2—O1	1.4781 (16)
Na1—O1	2.4745 (18)		
O3—Li1—O5 ⁱ	110.80 (19)	O1—Na1—Na1 ^{vi}	122.09 (5)
O3—Li1—O5 ⁱⁱ	110.80 (19)	O4 ^v —Na1—Na1 ^{vi}	46.13 (4)
O5 ⁱ —Li1—O5 ⁱⁱ	108.1 (2)	O2—Na1—Na1 ^{iv}	101.65 (6)
O3—Li1—O5 ⁱⁱⁱ	110.80 (19)	O6 ^{iv} —Na1—Na1 ^{iv}	39.26 (5)
O5 ⁱ —Li1—O5 ⁱⁱⁱ	108.1 (2)	O6—Na1—Na1 ^{iv}	84.99 (5)
O5 ⁱⁱ —Li1—O5 ⁱⁱⁱ	108.1 (2)	O5—Na1—Na1 ^{iv}	123.70 (5)
O3—Li1—Na1 ⁱ	126.29 (8)	O1—Na1—Na1 ^{iv}	142.09 (4)
O5 ⁱ —Li1—Na1 ⁱ	34.22 (10)	O4 ^v —Na1—Na1 ^{iv}	46.13 (4)
O5 ⁱⁱ —Li1—Na1 ⁱ	73.93 (13)	Na1 ^{vi} —Na1—Na1 ^{iv}	60.0
O5 ⁱⁱⁱ —Li1—Na1 ⁱ	118.2 (3)	O2—Na1—Li1 ^{xi}	72.56 (5)
O3—Li1—Na1 ⁱⁱⁱ	126.29 (8)	O6 ^{iv} —Na1—Li1 ^{xi}	167.19 (6)
O5 ⁱ —Li1—Na1 ⁱⁱⁱ	73.93 (13)	O6—Na1—Li1 ^{xi}	104.94 (7)
O5 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	118.2 (3)	O5—Na1—Li1 ^{xi}	26.85 (5)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱⁱ	34.22 (10)	O1—Na1—Li1 ^{xi}	75.37 (9)
Na1 ⁱ —Li1—Na1 ⁱⁱⁱ	88.54 (12)	O4 ^v —Na1—Li1 ^{xi}	97.99 (9)
O3—Li1—Na1 ⁱⁱ	126.29 (8)	Na1 ^{vi} —Na1—Li1 ^{xi}	105.97 (4)
O5 ⁱ —Li1—Na1 ⁱⁱ	118.2 (3)	Na1 ^{iv} —Na1—Li1 ^{xi}	142.53 (8)
O5 ⁱⁱ —Li1—Na1 ⁱⁱ	34.22 (10)	O3—S1—O2 ^{vii}	110.10 (8)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	73.93 (13)	O3—S1—O2	110.10 (8)
Na1 ⁱ —Li1—Na1 ⁱⁱ	88.54 (12)	O2 ^{vii} —S1—O2	108.83 (8)
Na1 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	88.54 (12)	O3—S1—O2 ^{viii}	110.10 (8)
O2—Na1—O6 ^{iv}	94.65 (7)	O2 ^{vii} —S1—O2 ^{viii}	108.83 (8)
O2—Na1—O6	171.96 (7)	O2—S1—O2 ^{viii}	108.83 (8)
O6 ^{iv} —Na1—O6	87.63 (9)	O4—S2—O1 ^{ix}	109.66 (7)
O2—Na1—O5	94.28 (6)	O4—S2—O1 ^x	109.66 (7)
O6 ^{iv} —Na1—O5	162.35 (7)	O1 ^{ix} —S2—O1 ^x	109.28 (7)
O6—Na1—O5	85.62 (7)	O4—S2—O1	109.66 (7)
O2—Na1—O1	88.05 (7)	O1 ^{ix} —S2—O1	109.28 (7)
O6 ^{iv} —Na1—O1	104.07 (6)	O1 ^x —S2—O1	109.28 (7)
O6—Na1—O1	83.92 (6)	S2—O1—Na1	131.18 (9)
O5—Na1—O1	91.41 (6)	S1—O2—Na1	126.18 (10)
O2—Na1—O4 ^v	102.93 (7)	S1—O3—Li1	180.0
O6 ^{iv} —Na1—O4 ^v	85.39 (6)	S2—O4—Na1 ^{xii}	126.84 (6)

O6—Na1—O4 ^v	84.92 (6)	S2—O4—Na1 ^{xiii}	126.84 (6)
O5—Na1—O4 ^v	77.80 (6)	Na1 ^{xii} —O4—Na1 ^{xiii}	87.75 (8)
O1—Na1—O4 ^v	165.02 (5)	S2—O4—Na1 ⁱ	126.84 (6)
O2—Na1—Na1 ^{vi}	149.02 (5)	Na1 ^{xii} —O4—Na1 ⁱ	87.75 (8)
O6 ^{iv} —Na1—Na1 ^{vi}	85.31 (5)	Na1 ^{xiii} —O4—Na1 ⁱ	87.75 (8)
O6—Na1—Na1 ^{vi}	38.80 (5)	Li1 ^{xi} —O5—Na1	118.93 (13)
O5—Na1—Na1 ^{vi}	79.22 (5)	Na1 ^{vi} —O6—Na1	101.94 (8)

Symmetry codes: (i) $x+1/3, x-y+2/3, z+1/6$; (ii) $-y+4/3, -x+2/3, z+1/6$; (iii) $-x+y+1/3, y-1/3, z+1/6$; (iv) $-x+y, -x, z$; (v) $-y+2/3, -x+1/3, z-1/6$; (vi) $-y, x-y, z$; (vii) $-y+1, x-y, z$; (viii) $-x+y+1, -x+1, z$; (ix) $-x+y, -x+1, z$; (x) $-y+1, x-y+1, z$; (xi) $-y+2/3, -x+4/3, z-1/6$; (xii) $-x+y+1/3, y+2/3, z+1/6$; (xiii) $-y+1/3, -x+2/3, z+1/6$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O6—H6 <i>A</i> ···O2 ^{xiii}	0.77 (5)	2.00 (5)	2.764 (11)	170 (5)
O6—H6 <i>B</i> ···O1	0.83 (4)	2.15 (4)	2.937 (7)	157 (4)
O5—H5 <i>B</i> ···O1 ^{xiv}	0.79 (4)	1.92 (4)	2.694 (7)	165 (4)
O5—H5 <i>A</i> ···O2 ^{ix}	0.89 (4)	1.97 (4)	2.828 (6)	163 (3)

Symmetry codes: (ix) $-x+y, -x+1, z$; (xiii) $-y+1/3, -x+2/3, z+1/6$; (xiv) $x-1/3, x-y+1/3, z-1/6$.

(Na₃Li₂SO₄·6H₂O-293K)

Crystal data

H₁₂LiNa₃O₁₄S₂

M_r = 376.13

Trigonal, *R*3*c*:*H*

a = 8.457 (7) Å

c = 30.33 (3) Å

V = 1879 (4) Å³

Z = 6

F(000) = 1152

D_x = 1.995 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 5111 reflections

θ = 2.9–27.1°

μ = 0.60 mm⁻¹

T = 293 K

Needle, colourless

0.3 × 0.15 × 0.1 mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4
mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration
Coppens (1970)

T_{min} = 0.517, *T_{max}* = 0.844

1376 measured reflections

730 independent reflections

695 reflections with *I* > 2σ(*I*)

R_{int} = 0.054

θ_{max} = 27.1°, θ_{min} = 3.9°

h = -9→10

k = -6→10

l = -38→35

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.038

wR(*F*²) = 0.105

S = 1.11

730 reflections

78 parameters

5 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0771*P*)² + 1.3675*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.33 e Å⁻³

Δρ_{min} = -0.47 e Å⁻³

Extinction correction: SHELXL2018/3

(Sheldrick 2015),

*F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.0054 (14)

Absolute structure: Classical Flack method
 preferred over Parsons because s.u. lower
 Absolute structure parameter: -0.3 (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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.666667	0.333333	0.1539 (4)	0.026 (3)
Na1	0.2353 (3)	0.2672 (3)	0.06061 (9)	0.0300 (5)
S1	0.666667	0.333333	0.04301 (5)	0.0167 (4)
S2	0.333333	0.666667	0.12572 (5)	0.0169 (4)
O1	0.3912 (5)	0.5387 (4)	0.10917 (11)	0.0263 (7)
O2	0.5187 (4)	0.3622 (5)	0.02643 (11)	0.0291 (7)
O3	0.666667	0.333333	0.0906 (2)	0.0365 (18)
O4	0.333333	0.666667	0.1745 (2)	0.0250 (13)
O5	0.1454 (5)	0.4298 (4)	0.00960 (11)	0.0256 (7)
H5A	0.059 (6)	0.440 (9)	0.018 (2)	0.035 (17)*
H5B	0.096 (9)	0.354 (8)	-0.0099 (18)	0.039 (16)*
O6	-0.0302 (5)	0.2083 (4)	0.10168 (12)	0.0290 (7)
H6B	-0.001 (11)	0.317 (3)	0.101 (3)	0.05 (2)*
H6A	-0.030 (11)	0.173 (10)	0.1268 (10)	0.042 (18)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.027 (4)	0.027 (4)	0.025 (7)	0.014 (2)	0.000	0.000
Na1	0.0298 (9)	0.0331 (10)	0.0285 (9)	0.0167 (8)	0.0058 (7)	0.0065 (7)
S1	0.0188 (6)	0.0188 (6)	0.0127 (8)	0.0094 (3)	0.000	0.000
S2	0.0173 (6)	0.0173 (6)	0.0161 (9)	0.0087 (3)	0.000	0.000
O1	0.0312 (17)	0.0265 (16)	0.0266 (16)	0.0185 (14)	-0.0024 (12)	-0.0045 (12)
O2	0.0261 (17)	0.0360 (17)	0.0297 (15)	0.0189 (14)	0.0011 (12)	0.0040 (13)
O3	0.048 (3)	0.048 (3)	0.013 (3)	0.0242 (15)	0.000	0.000
O4	0.029 (2)	0.029 (2)	0.017 (3)	0.0146 (11)	0.000	0.000
O5	0.0265 (16)	0.0226 (15)	0.0271 (14)	0.0118 (13)	0.0003 (11)	-0.0005 (10)
O6	0.0351 (19)	0.0276 (18)	0.0243 (15)	0.0156 (16)	0.0013 (12)	0.0008 (13)

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

Li1—O3	1.920 (15)	Na1—O4 ^v	2.671 (5)
Li1—O5 ⁱ	1.953 (6)	Na1—Na1 ^{iv}	3.702 (5)
Li1—O5 ⁱⁱ	1.953 (6)	Na1—Na1 ^{vi}	3.702 (5)
Li1—O5 ⁱⁱⁱ	1.953 (6)	S1—O3	1.443 (6)
Li1—Na1 ⁱⁱ	3.775 (8)	S1—O2	1.477 (3)

Li1—Na1 ⁱⁱⁱ	3.775 (8)	S1—O2 ^{vii}	1.477 (3)
Li1—Na1 ⁱ	3.775 (8)	S1—O2 ^{viii}	1.477 (3)
Na1—O2	2.354 (4)	S2—O4	1.479 (6)
Na1—O6 ^{iv}	2.372 (4)	S2—O1 ^{ix}	1.480 (3)
Na1—O6	2.392 (4)	S2—O1 ^x	1.480 (3)
Na1—O5	2.431 (4)	S2—O1	1.480 (3)
Na1—O1	2.481 (4)		
O3—Li1—O5 ⁱ	110.3 (4)	O1—Na1—Na1 ^{iv}	142.12 (9)
O3—Li1—O5 ⁱⁱ	110.3 (4)	O4 ^v —Na1—Na1 ^{iv}	46.12 (9)
O5 ⁱ —Li1—O5 ⁱⁱ	108.6 (4)	O2—Na1—Na1 ^{vi}	149.12 (10)
O3—Li1—O5 ⁱⁱⁱ	110.3 (4)	O6 ^{iv} —Na1—Na1 ^{vi}	85.24 (9)
O5 ⁱ —Li1—O5 ⁱⁱⁱ	108.6 (4)	O6—Na1—Na1 ^{vi}	38.80 (10)
O5 ⁱⁱ —Li1—O5 ⁱⁱⁱ	108.6 (4)	O5—Na1—Na1 ^{vi}	79.04 (11)
O3—Li1—Na1 ⁱⁱ	126.13 (16)	O1—Na1—Na1 ^{vi}	122.00 (10)
O5 ⁱ —Li1—Na1 ⁱⁱ	118.8 (5)	O4 ^v —Na1—Na1 ^{vi}	46.12 (9)
O5 ⁱⁱ —Li1—Na1 ⁱⁱ	34.45 (19)	Na1 ^{iv} —Na1—Na1 ^{vi}	60.0
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱ	74.2 (2)	O2—Na1—Li1 ^{xi}	72.81 (11)
O3—Li1—Na1 ⁱⁱⁱ	126.13 (16)	O6 ^{iv} —Na1—Li1 ^{xi}	167.34 (12)
O5 ⁱ —Li1—Na1 ⁱⁱⁱ	74.2 (2)	O6—Na1—Li1 ^{xi}	104.87 (13)
O5 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	118.8 (5)	O5—Na1—Li1 ^{xi}	27.04 (10)
O5 ⁱⁱⁱ —Li1—Na1 ⁱⁱⁱ	34.45 (19)	O1—Na1—Li1 ^{xi}	75.20 (18)
Na1 ⁱⁱ —Li1—Na1 ⁱⁱⁱ	88.8 (2)	O4 ^v —Na1—Li1 ^{xi}	98.10 (19)
O3—Li1—Na1 ⁱ	126.13 (16)	Na1 ^{iv} —Na1—Li1 ^{xi}	142.67 (16)
O5 ⁱ —Li1—Na1 ⁱ	34.45 (19)	Na1 ^{vi} —Na1—Li1 ^{xi}	105.96 (7)
O5 ⁱⁱ —Li1—Na1 ⁱ	74.2 (2)	O3—S1—O2	109.90 (16)
O5 ⁱⁱⁱ —Li1—Na1 ⁱ	118.8 (5)	O3—S1—O2 ^{vii}	109.90 (16)
Na1 ⁱⁱ —Li1—Na1 ⁱ	88.8 (2)	O2—S1—O2 ^{vii}	109.04 (16)
Na1 ⁱⁱⁱ —Li1—Na1 ⁱ	88.8 (2)	O3—S1—O2 ^{viii}	109.90 (16)
O2—Na1—O6 ^{iv}	94.56 (13)	O2—S1—O2 ^{viii}	109.04 (16)
O2—Na1—O6	171.91 (15)	O2 ^{vii} —S1—O2 ^{viii}	109.04 (16)
O6 ^{iv} —Na1—O6	87.53 (17)	O4—S2—O1 ^{ix}	109.82 (15)
O2—Na1—O5	94.58 (13)	O4—S2—O1 ^x	109.82 (15)
O6 ^{iv} —Na1—O5	162.10 (14)	O1 ^{ix} —S2—O1 ^x	109.13 (15)
O6—Na1—O5	85.57 (14)	O4—S2—O1	109.82 (15)
O2—Na1—O1	88.07 (14)	O1 ^{ix} —S2—O1	109.12 (15)
O6 ^{iv} —Na1—O1	104.17 (14)	O1 ^x —S2—O1	109.12 (15)
O6—Na1—O1	83.84 (12)	S2—O1—Na1	131.4 (2)
O5—Na1—O1	91.50 (13)	S1—O2—Na1	126.6 (2)
O2—Na1—O4 ^v	103.02 (15)	S1—O3—Li1	180.0
O6 ^{iv} —Na1—O4 ^v	85.33 (14)	S2—O4—Na1 ^{xii}	126.84 (13)
O6—Na1—O4 ^v	84.92 (14)	S2—O4—Na1 ^{xiii}	126.84 (13)
O5—Na1—O4 ^v	77.62 (14)	Na1 ^{xii} —O4—Na1 ^{xiii}	87.75 (19)
O1—Na1—O4 ^v	164.92 (11)	S2—O4—Na1 ⁱ	126.84 (13)
O2—Na1—Na1 ^{iv}	101.59 (12)	Na1 ^{xii} —O4—Na1 ⁱ	87.75 (19)
O6 ^{iv} —Na1—Na1 ^{iv}	39.20 (10)	Na1 ^{xiii} —O4—Na1 ⁱ	87.75 (19)

O6—Na1—Na1 ^{iv}	84.96 (9)	Li1 ^{xi} —O5—Na1	118.5 (3)
O5—Na1—Na1 ^{iv}	123.52 (10)	Na1 ^{vi} —O6—Na1	102.00 (15)

Symmetry codes: (i) $x+1/3, x-y+2/3, z+1/6$; (ii) $-y+4/3, -x+2/3, z+1/6$; (iii) $-x+y+1/3, y-1/3, z+1/6$; (iv) $-x+y, -x, z$; (v) $-y+2/3, -x+1/3, z-1/6$; (vi) $-y, x-y, z$; (vii) $-y+1, x-y, z$; (viii) $-x+y+1, -x+1, z$; (ix) $-x+y, -x+1, z$; (x) $-y+1, x-y+1, z$; (xi) $-y+2/3, -x+4/3, z-1/6$; (xii) $-x+y+1/3, y+2/3, z+1/6$; (xiii) $-y+1/3, -x+2/3, z+1/6$.