

Trilithium thioarsenate octahydrate

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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{As}-\text{S}) = 0.001$ Å;
R factor = 0.028; wR factor = 0.057; data-to-parameter ratio = 22.1.

The title compound, $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$, is built up from infinite cationic $[\text{Li}_3(\text{H}_2\text{O})_8]^{3+}$ chains which extend along [001] and are cross-linked by isolated tetrahedral AsS_4^{3-} anions via $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonds. Two Li and two As atoms lie on special positions with site symmetries $\bar{1}$ ($1 \times \text{Li}$) and 2 ($1 \times \text{Li}$ and $2 \times \text{As}$). The $[\text{Li}_3(\text{H}_2\text{O})_8]^{3+}$ chain contains four independent Li atoms of which two are in octahedral and two in tetrahedral coordination by water O atoms. An outstanding feature of this chain is a linear group of three edge-sharing LiO_6 octahedra to both ends of which two LiO_4 tetrahedra are attached by face-sharing. Such groups of composition Li_5O_{16} are linked into branched chains by means of a further LiO_4 tetrahedron sharing vertices with four adjacent LiO_6 octahedra. The Li—O bonds range from 1.876 (5) to 2.054 (6) Å for the LiO_4 tetrahedra and from 2.026 (5) to 2.319 (5) Å for the LiO_6 octahedra. The two independent AsS_4^{3-} anions have As—S bond lengths ranging from 2.1482 (6) to 2.1677 (6) Å [$\langle \text{As}-\text{S} \rangle = 2.161$ (10) Å]. The eight independent water molecules of the structure donate 16 relatively straight $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonds to all S atoms of the AsS_4 tetrahedra [$\langle \text{O} \cdots \text{S} \rangle = 3.295$ (92) Å]. Seven water molecules are in distorted tetrahedral coordination by two Li and two S; one water molecule has a flat pyramidal coordination by one Li and two S. At variance with related compounds like Schlippe's salt, $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, there are neither alkali-sulfur bonds nor $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in the structure.

Related literature

For crystal structures of related chalcogenosalt hydrates based on isolated tetrahedral XY_4 anions, see: Mereiter *et al.* (1979, 1982, 1983); Krebs *et al.* (1990); Krebs & Jacobsen (1976); Krebs & Huerter (1980); Schiwy *et al.* (1973); Melullis & Dehnen (2007), Ruzin *et al.* (2006, 2008). For the prototype compound Schlippe's Salt, $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, see: Schlippe (1821). For the synthesis of the title compound and early crystallographic data, see: Rémy & Bachet (1968). For the synthesis and crystal structure of $\text{Ba}_3(\text{AsS}_4)_2 \cdot 7\text{H}_2\text{O}$ as a precursor of the title compound, see: Mereiter & Preisinger

(1992). For the crystal structure of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, see: Preisinger *et al.* (1982). For a review on $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonds in salt hydrates, see: Mikenda *et al.* (1989).

Experimental

Crystal data

$\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$	$V = 1375.5$ (5) Å ³
$M_r = 368.11$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.036$ (2) Å	$\mu = 3.09$ mm ⁻¹
$b = 10.064$ (2) Å	$T = 297$ K
$c = 14.264$ (3) Å	$0.30 \times 0.27 \times 0.25$ mm
$\beta = 107.30$ (1)°	

Data collection

Philips PW1100 four-circle diffractometer	4001 independent reflections
Absorption correction: for a sphere	2913 reflections with $I > 2\sigma(I)$
$\mu R = 0.45$	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.51$, $T_{\text{max}} = 0.54$	3 standard reflections every 60 min
5729 measured reflections	intensity decay: 2.0%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	181 parameters
$wR(F^2) = 0.057$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.61$ e Å ⁻³
4001 reflections	$\Delta\rho_{\text{min}} = -0.36$ e Å ⁻³

Table 1

Selected bond lengths (Å).

Li1—O2	2.130 (2)	Li3—O1	2.009 (4)
Li1—O1	2.203 (2)	Li4—O8	1.876 (5)
Li1—O3	2.274 (2)	Li4—O5	1.957 (5)
Li2—O3	2.026 (4)	Li4—O6	1.990 (6)
Li2—O2	2.127 (5)	Li4—O7	2.054 (6)
Li2—O5	2.202 (4)	As1—S2	2.1482 (6)
Li2—O4	2.225 (5)	As1—S1	2.1711 (6)
Li2—O6	2.271 (5)	As2—S4	2.1574 (6)
Li2—O7	2.319 (5)	As2—S3	2.1677 (6)
Li3—O4	1.991 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1—H1A \cdots S1 ⁱ	0.80	2.49	3.262 (2)	163
O1—H1B \cdots S4 ⁱⁱ	0.80	2.51	3.287 (2)	163
O2—H2A \cdots S1 ⁱⁱⁱ	0.80	2.76	3.531 (2)	162
O2—H2B \cdots S2	0.80	2.37	3.167 (2)	173
O3—H3A \cdots S3 ^{iv}	0.80	2.61	3.400 (2)	168
O3—H3B \cdots S4	0.80	2.39	3.190 (2)	173
O4—H4A \cdots S1 ⁱⁱⁱ	0.80	2.51	3.240 (2)	153
O4—H4B \cdots S3 ^v	0.80	2.42	3.207 (2)	170
O5—H5A \cdots S1	0.80	2.45	3.247 (2)	172
O5—H5B \cdots S2 ⁱⁱⁱ	0.80	2.50	3.303 (2)	177
O6—H6A \cdots S3	0.80	2.57	3.354 (2)	168
O6—H6B \cdots S4 ^{iv}	0.80	2.54	3.307 (2)	162
O7—H7A \cdots S1 ^{vi}	0.80	2.49	3.244 (2)	157
O7—H7B \cdots S3	0.80	2.58	3.333 (2)	157
O8—H8A \cdots S2 ^{vii}	0.80	2.50	3.253 (2)	157
O8—H8B \cdots S3 ^{vi}	0.80	2.61	3.394 (2)	166

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

Data collection: *Philips PW1100 software* (Hornstra & Vossers, 1973); cell refinement: *LLSQ* (Mereiter, 1992); data reduction: *PWD* (Mereiter, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXL97* and *pubCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PJ2002).

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supplementary materials

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Comment

The title compound, $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$, belongs to a group of alkali chalcogenosalt hydrates with tetrahedral XY_4 anions, $X = \text{P(V)}$, As(V) , Sb(V) , Ge(IV) , Sn(IV) and $Y = \text{S}^{2-}$, Se^{2-} , Te^{2-} , of which Schlippe's salt, $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ (Schlippe, 1821; Mereiter *et al.*, 1979) can be considered as the prototype. Other representatives with known crystal structures are $\text{Na}_3\text{PS}_4 \cdot 8\text{H}_2\text{O}$ (Mereiter *et al.*, 1983), $\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ (Mereiter *et al.*, 1982), $\text{Na}_3\text{AsSe}_4 \cdot 9\text{H}_2\text{O}$ (Krebs *et al.*, 1990), $\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$ (Schiwy *et al.*, 1973), $\text{Na}_4\text{GeSe}_4 \cdot 14\text{H}_2\text{O}$ (Krebs & Jacobsen, 1976), $\text{Na}_4\text{SnSe}_4 \cdot 16\text{H}_2\text{O}$ (Krebs & Huerter, 1980), $\text{K}_4\text{GeSe}_4 \cdot 4\text{H}_2\text{O}$ (Melullis & Dehnen, 2007), $\text{Rb}_4\text{SnTe}_4 \cdot 2\text{H}_2\text{O}$ (Ruzin *et al.*, 2006), $\text{K}_4\text{SnS}_4 \cdot 4\text{H}_2\text{O}$ (Ruzin *et al.*, 2008), to mention only some examples.

In context with previous work (Mereiter & Preisinger, 1992) the title compound $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ was prepared and its crystal structure was determined. An early report on the synthesis and crystal data of this compound was given by Rémy & Bachet (1968).

$\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ crystallizes in the infrequent centrosymmetric monoclinic space group $P2_1/c$ (No. 13). The crystal structure contains four independent Li atoms, two independent AsS_4 tetrahedra and eight independent water molecules in the asymmetric unit. Li1 lies on a centre of inversion while Li3, As1, and As2 are located on twofold axes. All other constituents comprising Li2 and Li4, four S, and eight H_2O are in general position. A view of a characteristic part of the crystal structure containing all constituents is shown in Fig. 1. All lithium atoms are exclusively coordinated by the oxygen atoms of the water molecules but not by any sulfur atom. Li1 and Li2 form $\text{Li}(\text{H}_2\text{O})_6$ octahedra while Li3 and Li4 form $\text{Li}(\text{H}_2\text{O})_4$ tetrahedra. The $\text{Li1}(\text{H}_2\text{O})_6$ octahedron shares edges with two adjacent $\text{Li2}(\text{H}_2\text{O})_6$ octahedra, and they in turn share faces with two $\text{Li4}(\text{H}_2\text{O})_4$ tetrahedra. This gives rise to characteristic polyhedral pentamers $\text{Li}_5(\text{H}_2\text{O})_{16}$ which are linked by the $\text{Li3}(\text{H}_2\text{O})_4$ tetrahedra *via* vertex sharing with four adjacent $\text{Li}(\text{H}_2\text{O})_6$ octahedra to form infinite branched chains of the composition $\text{Li}_6(\text{H}_2\text{O})_{16}$ or $\text{Li}_3(\text{H}_2\text{O})_8$ (Figs. 2 and 3). The chains extend along [001] and have the $\text{Li}_5(\text{H}_2\text{O})_{16}$ fragments oriented in a criss-cross fashion (Figs. 3 and 4). Embedded between the chains are the tetrahedral AsS_4^{3-} anions, which are anchored exclusively by $\text{O}—\text{H}\cdots\text{S}$ type hydrogen bonds donated by the water molecules. The sulfur atoms receive either three (S2, S4) or five (S1, S3) hydrogen bonds so that each AsS_4^{3-} anion receives 16 hydrogen bonds of which 8 are symmetry redundant. The eight different water molecules of the structure have mainly distorted tetrahedral coordination environments by two Li cations and two S atoms as hydrogen bond acceptors. Only the water molecule $\text{H}_2\text{O}8$ differs from this behaviour by being bonded to only one Li and two S atoms within a distorted trigonal pyramidal coordination.

The Li—O bonds range from 2.026 (5) to 2.319 (5) Å for the LiO_6 octahedra and from 1.876 (5) to 2.054 (6) Å for the LiO_4 tetrahedra (Table 1). The mean Li—O bond lengths are 2.202 (65), 2.195 (105), 2.000 (10) and 1.969 (74) Å for Li1 through Li4. The coordination figures of Li1 and Li3 are relatively regular (O—Li—O bond angles for Li1O_6 81.84 (6)–98.16 (6)° and 180°, for Li3O_4 101.7 (2)–114.3 (3)°) while those of Li2 and Li4 are notably distorted due to the face-sharing link between them (O—Li—O bond angles for Li2O_6 72.7 (2)–100.6 (2)° and 167.3 (2)–174.8 (3)°, for Li4O_4

84.6 (2)–129.8 (2)°; $\text{Li2}\cdots\text{Li4} = 2.698$ (7) Å). The two independent AsS_4^{3-} anions have As—S bond distances from 2.1482 (6) to 2.1677 (6) Å, $\langle\text{As—S}\rangle = 2.161$ (10) Å. The two shorter As—S bonds in each tetrahedron are to sulfur atoms receiving three hydrogen bonds (S2, S4) while the longer As—S bonds are to sulfur atoms receiving five hydrogen bonds (S1, S3). The As—S bond lengths and the S—As—S bond angles (106.72 (3)–111.42 (2) and 106.15 (2)–112.69 (2)° for As1 and As2, respectively) show that the two tetrahedra are relatively regular. They agree in their dimensions with related thioarsenates (Mereiter *et al.*, 1982; Mereiter & Preisinger, 1992). The eight independent water molecules of the structure donate 16 relatively straight O—H \cdots S hydrogen bonds to all S atoms of the AsS_4 tetrahedra, $\text{O}\cdots\text{S} = 3.167$ (2) – 3.531 (2) Å, $\langle\text{O}\cdots\text{S}\rangle = 3.295$ (92) Å and $\text{O—H}\cdots\text{S} = 153$ –177° (Table 2; Figs. 2 and 3). These dimensions fit well into the pattern of O—H \cdots S hydrogen bonds in sulfosalt hydrates reported by Mikenda *et al.* (1989).

The structure of title compound $\text{Li}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ adds a new facet to the very diverse structural chemistry of the chalcogenosalt hydrates with tetrahedral XY_4 anions defined above. The two isochemical relatives of the title compound, $\text{Na}_3\text{PS}_4\cdot 8\text{H}_2\text{O}$ (Mereiter *et al.*, 1983) and $\text{Na}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ (Mereiter *et al.*, 1982), represent an isostructural pair built up from $\text{NaS}_2(\text{H}_2\text{O})_4$, $\text{NaS}(\text{H}_2\text{O})_5$ and $\text{Na}(\text{H}_2\text{O})_6$ octahedra which form together with the PS_4/AsS_4 tetrahedra undulating layers. The PS_4/AsS_4 tetrahedron is linked with three S atoms to the Na cations. The water molecules are mostly bonded to two Na and donate pairs of O—H \cdots S hydrogen bonds. One water molecule is bonded to only one Na and accepts in compensation an O—H \cdots O hydrogen bond. Schlippe's salt, $\text{Na}_3\text{SbS}_4\cdot 9\text{H}_2\text{O}$ (Mereiter *et al.*, 1979) and the isostructural selenoarsenate (Krebs *et al.*, 1990) contain per formula unit one water more than the title compound. They are built up from tripledeckers of facesharing octahedra - namely a $\text{Na}(\text{H}_2\text{O})_6$ octahedron which shares two opposite faces with a $\text{Na}(\text{H}_2\text{O})_6$ and a $\text{NaS}_3(\text{H}_2\text{O})_3$ octahedron. The tetrahedral SbS_4 anion is bonded with three S atoms to three tripledeckers and links them into a complicated framework of cubic symmetry. Here again only one S atom is not cation-bonded and the structure contains independent five O—H \cdots S and one O—H \cdots O bonds. The compounds $\text{Na}_4\text{SnS}_4\cdot 14\text{H}_2\text{O}$ (Schiwy *et al.*, 1973), $\text{Na}_4\text{GeSe}_4\cdot 14\text{H}_2\text{O}$ (Krebs & Jacobsen, 1976), and $\text{Na}_4\text{SnSe}_4\cdot 16\text{H}_2\text{O}$ (Krebs & Huerter, 1980) can be seen as variants of the Na-water triple deckers in Schlippe's salt and only in $\text{Na}_4\text{SnSe}_4\cdot 16\text{H}_2\text{O}$ these triple deckers form Na—H $_2\text{O}$ polymers without any Na-chalcogen bonds. Alkali sulfosalts with cations larger than Na - *e.g.* $\text{K}_4\text{GeSe}_4\cdot 4\text{H}_2\text{O}$ (Melullis & Dehnen, 2007), $\text{Rb}_4\text{SnTe}_4\cdot 2\text{H}_2\text{O}$ (Ruzin *et al.*, 2006), or $\text{K}_4\text{SnS}_4\cdot 4\text{H}_2\text{O}$ (Ruzin *et al.*, 2008) - contain less water per cation and adopt alkali-water structures with higher coordination numbers than 6 for the cation sites and they involve therefore increasingly alkali-chalcogen bonds. Although not a sulfo-salt, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ may be mentioned here for comparison with $\text{Li}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ because it is built up from octahedral chains $\text{Na}(\text{H}_2\text{O})_5$ (corner-sharing spiral chains) and $\text{Na}(\text{H}_2\text{O})_4$ (edge-sharing spiral chains) held together by isolated sulfide ions *via* many O—H \cdots S bonds and by some O—H \cdots O bonds (Preisinger *et al.*, 1982).

Experimental

The title compound was prepared by mixing dilute aqueous solutions of $\text{Ba}_3(\text{AsS}_4)_2\cdot 7\text{H}_2\text{O}$ (Mereiter & Preisinger, 1992) and $\text{Li}_2\text{SO}_4\cdot \text{H}_2\text{O}$ in stoichiometric amounts. After removing BaSO_4 by filtration, the solution was preconcentrated in a rotavapor under reduced pressure and then filtered. Crystallization by room temperature evaporation in an exsiccator over conc. H_2SO_4 as desiccant gave the desired $\text{Li}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ in the form of colourless prisms. For structure analysis, a fragment was rounded to an oval by turning it on wet filter paper. Another preparation method for $\text{Li}_3\text{AsS}_4\cdot 8\text{H}_2\text{O}$ was reported by Rémy & Bachet (1968).

Refinement

All water molecules were idealized to have $\text{O—H} = 0.80$ Å and $\text{H—O—H} = 105.0^\circ$ and were then refined as rigid groups using AFIX 6 of *SHELXL97* (Sheldrick, 2008). A common U_{iso} for the two H-atoms of each water molecule was used and

refined.

Computing details

Data collection: *Philips PW1100 software* (Hornstra & Vossers, 1973); cell refinement: *LLSQ* (Mereiter, 1992); data reduction: *PWD* (Mereiter, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *pubCIF* (Westrip, 2010).

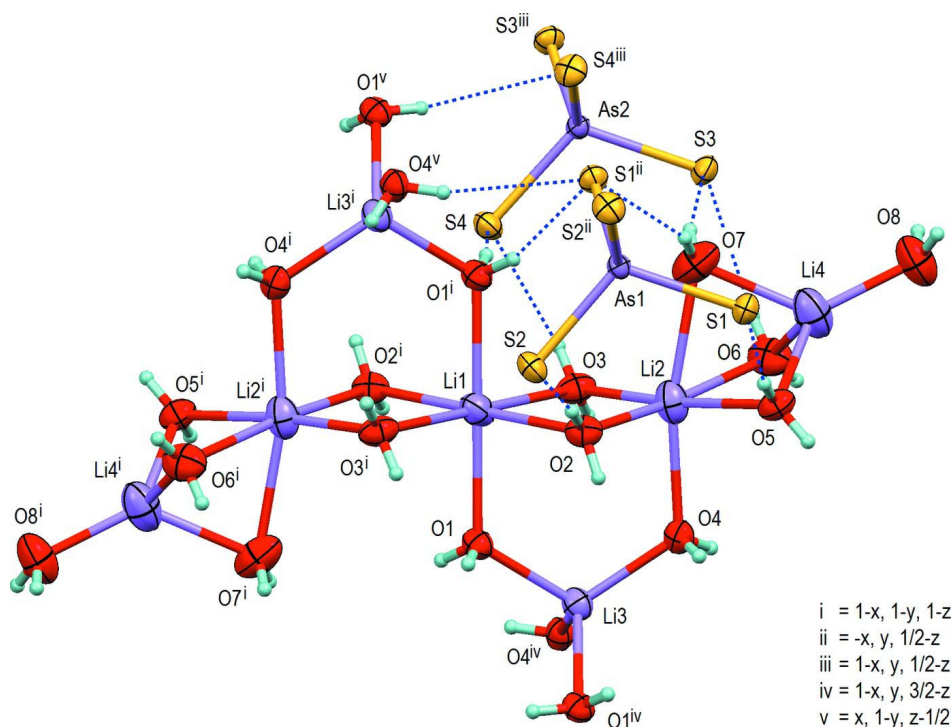


Figure 1

A representative part of the structure of $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level. Symmetry codes are given on the lower right. Hydrogen bonds in this assembly are shown as dashed lines.

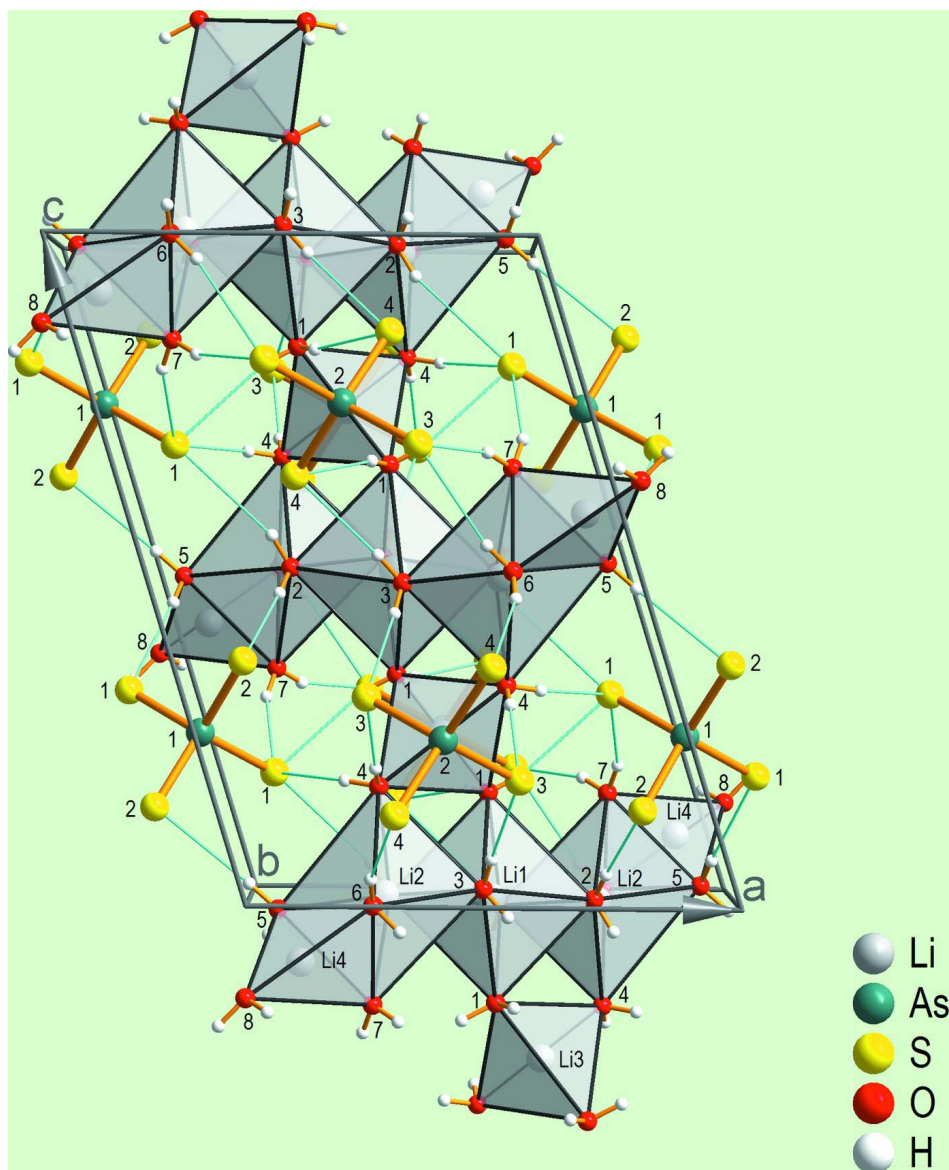


Figure 2

A packing diagram of $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ viewed along the b -axis showing also the hydrogen bonds. Only the label numbers are given for As, S, and O atoms.

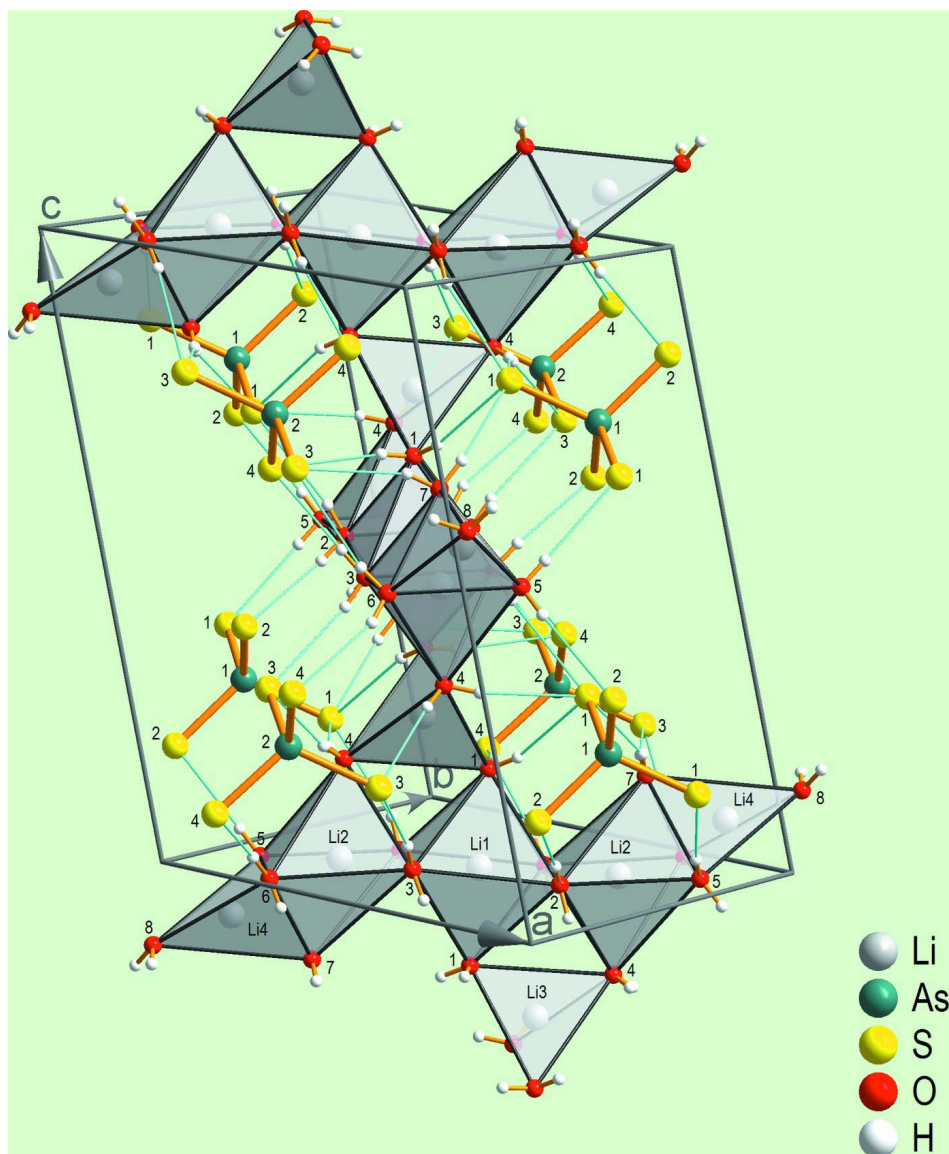
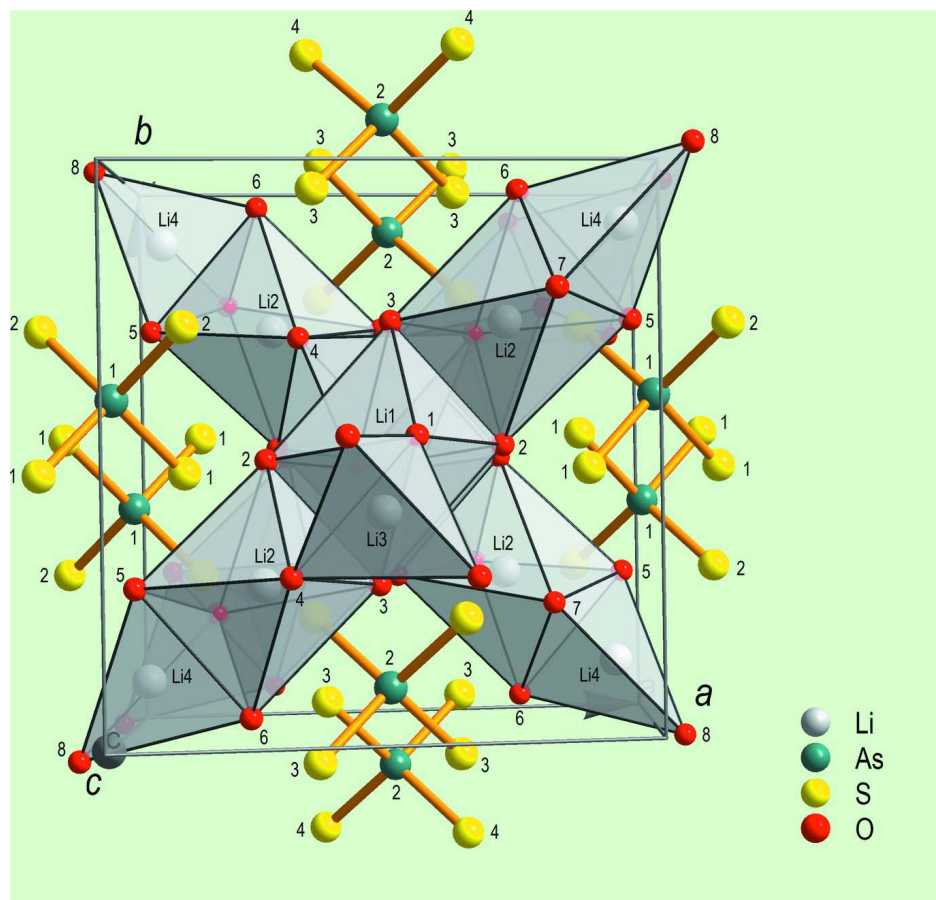


Figure 3

A packing diagram of $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ viewed approximately along to $[1\bar{1}0]$ showing also the hydrogen bonds. Only the label numbers are given for As, S, and O atoms.


Figure 4

View of the structure of $\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$ along $[001]$. H-atoms omitted for clarity. Li3, As1 and As2 lie on twofold axes parallel $[010]$, and Li1 on $\bar{1}$ at $x, y, z = 1/2, 1/2, 1/2$.

Trilithium thioarsenate octahydrate

Crystal data

$\text{Li}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$

$M_r = 368.11$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 10.036\ (2)\ \text{\AA}$

$b = 10.064\ (2)\ \text{\AA}$

$c = 14.264\ (3)\ \text{\AA}$

$\beta = 107.30\ (1)^\circ$

$V = 1375.5\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 744$

$D_x = 1.778\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 34 reflections

$\theta = 9.1\text{--}26.2^\circ$

$\mu = 3.09\ \text{mm}^{-1}$

$T = 297\ \text{K}$

Oval, colourless

$0.30 \times 0.27 \times 0.25\ \text{mm}$

Data collection

Philips PW1100 four-circle
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω - 2θ scans

Absorption correction: for a sphere

$\mu R = 0.45$

$T_{\min} = 0.51, T_{\max} = 0.54$

5729 measured reflections

4001 independent reflections

2913 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -14 \rightarrow 13$
 $k = -14 \rightarrow 14$

$l = 0 \rightarrow 20$
 3 standard reflections every 60 min
 intensity decay: 2.0%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.057$
 $S = 1.05$
 4001 reflections
 181 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.5909P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0081 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Li1	0.5000	0.5000	0.5000	0.0393 (13)
Li2	0.2821 (4)	0.7213 (4)	0.5102 (4)	0.0443 (10)
Li3	0.5000	0.5984 (5)	0.7500	0.0311 (11)
Li4	0.0724 (5)	0.8832 (5)	0.4126 (5)	0.0610 (14)
As1	0.0000	0.40273 (3)	0.2500	0.01865 (8)
As2	0.5000	0.91402 (2)	0.2500	0.01887 (8)
S1	-0.12581 (5)	0.53147 (5)	0.31185 (4)	0.02508 (11)
S2	0.13565 (5)	0.27910 (5)	0.36066 (4)	0.02849 (12)
S3	0.37068 (5)	1.03848 (5)	0.31147 (4)	0.02615 (12)
S4	0.64151 (6)	0.79087 (5)	0.35891 (4)	0.02873 (12)
O1	0.55849 (15)	0.47247 (15)	0.66032 (12)	0.0297 (3)
H1A	0.6400	0.4629	0.6874	0.054 (6)*
H1B	0.5239	0.4023	0.6655	0.054 (6)*
O2	0.28906 (17)	0.51048 (16)	0.50233 (12)	0.0330 (3)
H2A	0.2693	0.4923	0.5512	0.068 (8)*
H2B	0.2494	0.4564	0.4627	0.068 (8)*
O3	0.48739 (17)	0.72351 (17)	0.51911 (12)	0.0359 (4)
H3A	0.5233	0.7696	0.5654	0.077 (8)*
H3B	0.5211	0.7466	0.4775	0.077 (8)*
O4	0.33730 (16)	0.70514 (14)	0.67279 (12)	0.0303 (3)

H4A	0.2703	0.6689	0.6804	0.051 (6)*
H4B	0.3423	0.7745	0.7010	0.051 (6)*
O5	0.05507 (17)	0.72354 (16)	0.48637 (12)	0.0344 (4)
H5A	0.0167	0.6700	0.4459	0.059 (7)*
H5B	0.0110	0.7247	0.5248	0.059 (7)*
O6	0.2558 (2)	0.9454 (2)	0.49965 (14)	0.0486 (5)
H6A	0.2939	0.9720	0.4614	0.107 (11)*
H6B	0.2680	1.0022	0.5406	0.107 (11)*
O7	0.1906 (2)	0.7739 (2)	0.34519 (16)	0.0535 (5)
H7A	0.1517	0.7256	0.3009	0.112 (12)*
H7B	0.2329	0.8251	0.3220	0.112 (12)*
O8	-0.05671 (19)	1.0198 (2)	0.36351 (18)	0.0573 (6)
H8A	-0.0190	1.0806	0.3455	0.102 (11)*
H8B	-0.1288	1.0100	0.3210	0.102 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.035 (3)	0.041 (3)	0.041 (3)	0.003 (3)	0.010 (2)	0.012 (3)
Li2	0.035 (2)	0.038 (2)	0.059 (3)	0.0012 (18)	0.013 (2)	0.001 (2)
Li3	0.029 (3)	0.030 (3)	0.032 (3)	0.000	0.006 (2)	0.000
Li4	0.049 (3)	0.046 (2)	0.086 (4)	0.005 (2)	0.017 (3)	0.018 (3)
As1	0.01756 (13)	0.01845 (13)	0.01937 (15)	0.000	0.00463 (11)	0.000
As2	0.02138 (14)	0.01735 (13)	0.01920 (15)	0.000	0.00807 (11)	0.000
S1	0.0240 (2)	0.0256 (2)	0.0277 (3)	0.00128 (18)	0.0108 (2)	-0.0028 (2)
S2	0.0273 (3)	0.0254 (2)	0.0287 (3)	0.0044 (2)	0.0022 (2)	0.0044 (2)
S3	0.0294 (3)	0.0243 (2)	0.0287 (3)	0.00180 (19)	0.0148 (2)	-0.0032 (2)
S4	0.0294 (3)	0.0266 (2)	0.0286 (3)	0.0047 (2)	0.0063 (2)	0.0071 (2)
O1	0.0293 (8)	0.0294 (7)	0.0276 (8)	0.0006 (6)	0.0042 (6)	0.0006 (6)
O2	0.0358 (8)	0.0319 (8)	0.0293 (8)	-0.0075 (7)	0.0066 (7)	-0.0028 (7)
O3	0.0358 (9)	0.0438 (9)	0.0290 (9)	-0.0110 (7)	0.0110 (7)	-0.0023 (8)
O4	0.0314 (8)	0.0250 (7)	0.0365 (9)	-0.0023 (6)	0.0130 (7)	-0.0017 (6)
O5	0.0385 (9)	0.0360 (8)	0.0311 (9)	-0.0074 (7)	0.0140 (7)	-0.0056 (7)
O6	0.0590 (12)	0.0413 (9)	0.0406 (11)	-0.0078 (9)	0.0076 (10)	-0.0058 (9)
O7	0.0693 (14)	0.0463 (11)	0.0568 (13)	-0.0217 (10)	0.0367 (11)	-0.0157 (10)
O8	0.0377 (10)	0.0424 (11)	0.0836 (16)	0.0008 (9)	0.0052 (10)	0.0137 (11)

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

Li1—O2	2.130 (2)	As1—S1 ⁱⁱⁱ	2.1711 (6)
Li1—O2 ⁱ	2.130 (2)	As1—S1	2.1711 (6)
Li1—O1	2.203 (2)	As2—S4 ^{iv}	2.1574 (6)
Li1—O1 ⁱ	2.203 (2)	As2—S4	2.1574 (6)
Li1—O3	2.274 (2)	As2—S3	2.1677 (6)
Li1—O3 ⁱ	2.274 (2)	As2—S3 ^{iv}	2.1677 (6)
Li2—O3	2.026 (4)	O1—H1A	0.80
Li2—O2	2.127 (5)	O1—H1B	0.80
Li2—O5	2.202 (4)	O2—H2A	0.80
Li2—O4	2.225 (5)	O2—H2B	0.80
Li2—O6	2.271 (5)	O3—H3A	0.80

Li2—O7	2.319 (5)	O3—H3B	0.80
Li3—O4 ⁱⁱ	1.991 (3)	O4—H4A	0.80
Li3—O4	1.991 (3)	O4—H4B	0.80
Li3—O1	2.009 (4)	O5—H5A	0.80
Li3—O1 ⁱⁱ	2.009 (4)	O5—H5B	0.80
Li4—O8	1.876 (5)	O6—H6A	0.80
Li4—O5	1.957 (5)	O6—H6B	0.80
Li4—O6	1.990 (6)	O7—H7A	0.80
Li4—O7	2.054 (6)	O7—H7B	0.80
As1—S2 ⁱⁱⁱ	2.1482 (6)	O8—H8A	0.80
As1—S2	2.1482 (6)	O8—H8B	0.80
O2—Li1—O2 ⁱ	180.0	S4—As2—S3	112.69 (2)
O2—Li1—O1 ⁱ	92.91 (6)	S4 ^{iv} —As2—S3 ^{iv}	112.69 (2)
O2 ⁱ —Li1—O1 ⁱ	87.09 (6)	S4—As2—S3 ^{iv}	106.15 (2)
O2—Li1—O1	87.09 (6)	S3—As2—S3 ^{iv}	109.40 (3)
O2 ⁱ —Li1—O1	92.91 (6)	Li3—O1—Li1	122.93 (10)
O1 ⁱ —Li1—O1	180.0	Li3—O1—H1A	102.7
O2—Li1—O3 ⁱ	98.16 (6)	Li1—O1—H1A	115.8
O2 ⁱ —Li1—O3 ⁱ	81.84 (6)	Li3—O1—H1B	106.3
O1 ⁱ —Li1—O3 ⁱ	90.41 (6)	Li1—O1—H1B	102.6
O1—Li1—O3 ⁱ	89.59 (6)	H1A—O1—H1B	105.0
O2—Li1—O3	81.84 (6)	Li2—O2—Li1	95.65 (13)
O2 ⁱ —Li1—O3	98.16 (6)	Li2—O2—H2A	99.3
O1 ⁱ —Li1—O3	89.59 (6)	Li1—O2—H2A	120.5
O1—Li1—O3	90.41 (6)	Li2—O2—H2B	134.3
O3 ⁱ —Li1—O3	180.0	Li1—O2—H2B	104.1
O3—Li2—O2	88.03 (18)	H2A—O2—H2B	105.0
O3—Li2—O5	174.8 (3)	Li2—O3—Li1	94.22 (14)
O2—Li2—O5	92.89 (17)	Li2—O3—H3A	105.0
O3—Li2—O4	90.12 (18)	Li1—O3—H3A	130.2
O2—Li2—O4	88.84 (18)	Li2—O3—H3B	127.1
O5—Li2—O4	94.98 (19)	Li1—O3—H3B	98.5
O3—Li2—O6	95.14 (18)	H3A—O3—H3B	105.0
O2—Li2—O6	172.9 (3)	Li3—O4—Li2	121.68 (14)
O5—Li2—O6	83.40 (16)	Li3—O4—H4A	105.3
O4—Li2—O6	97.45 (19)	Li2—O4—H4A	102.5
O3—Li2—O7	98.6 (2)	Li3—O4—H4B	105.9
O2—Li2—O7	100.6 (2)	Li2—O4—H4B	114.8
O5—Li2—O7	76.20 (15)	H4A—O4—H4B	105.0
O4—Li2—O7	167.3 (2)	Li4—O5—Li2	80.7 (2)
O6—Li2—O7	72.74 (15)	Li4—O5—H5A	105.4
O4 ⁱⁱ —Li3—O4	114.7 (3)	Li2—O5—H5A	111.0
O4 ⁱⁱ —Li3—O1	110.23 (7)	Li4—O5—H5B	120.8
O4—Li3—O1	109.58 (7)	Li2—O5—H5B	130.7
O4 ⁱⁱ —Li3—O1 ⁱⁱ	109.58 (7)	H5A—O5—H5B	105.0
O4—Li3—O1 ⁱⁱ	110.23 (7)	Li4—O6—Li2	78.26 (19)
O1—Li3—O1 ⁱⁱ	101.7 (2)	Li4—O6—H6A	102.8
O8—Li4—O5	129.8 (3)	Li2—O6—H6A	107.9

O8—Li4—O6	114.2 (3)	Li4—O6—H6B	126.3
O5—Li4—O6	97.9 (3)	Li2—O6—H6B	132.2
O8—Li4—O7	130.4 (3)	H6A—O6—H6B	105.0
O5—Li4—O7	88.2 (2)	Li4—O7—Li2	75.9 (2)
O6—Li4—O7	84.6 (2)	Li4—O7—H7A	118.8
S2 ⁱⁱⁱ —As1—S2	109.21 (3)	Li2—O7—H7A	128.0
S2 ⁱⁱⁱ —As1—S1 ⁱⁱⁱ	111.42 (2)	Li4—O7—H7B	107.4
S2—As1—S1 ⁱⁱⁱ	109.04 (2)	Li2—O7—H7B	117.9
S2 ⁱⁱⁱ —As1—S1	109.04 (2)	H7A—O7—H7B	105.0
S2—As1—S1	111.42 (2)	Li4—O8—H8A	109.9
S1 ⁱⁱⁱ —As1—S1	106.72 (3)	Li4—O8—H8B	124.1
S4 ^{iv} —As2—S4	109.87 (4)	H8A—O8—H8B	105.0
S4 ^{iv} —As2—S3	106.15 (2)		

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

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>
O1—H1A \cdots S1 ^v	0.80	2.49	3.262 (2)	163
O1—H1B \cdots S4 ⁱ	0.80	2.51	3.287 (2)	163
O2—H2A \cdots S1 ^{vi}	0.80	2.76	3.531 (2)	162
O2—H2B \cdots S2	0.80	2.37	3.167 (2)	173
O3—H3A \cdots S3 ^{vii}	0.80	2.61	3.400 (2)	168
O3—H3B \cdots S4	0.80	2.39	3.190 (2)	173
O4—H4A \cdots S1 ^{vi}	0.80	2.51	3.240 (2)	153
O4—H4B \cdots S3 ^{viii}	0.80	2.42	3.207 (2)	170
O5—H5A \cdots S1	0.80	2.45	3.247 (2)	172
O5—H5B \cdots S2 ^{vi}	0.80	2.50	3.303 (2)	177
O6—H6A \cdots S3	0.80	2.57	3.354 (2)	168
O6—H6B \cdots S4 ^{vii}	0.80	2.54	3.307 (2)	162
O7—H7A \cdots S1 ⁱⁱⁱ	0.80	2.49	3.244 (2)	157
O7—H7B \cdots S3	0.80	2.58	3.333 (2)	157
O8—H8A \cdots S2 ^{ix}	0.80	2.50	3.253 (2)	157
O8—H8B \cdots S3 ⁱⁱⁱ	0.80	2.61	3.394 (2)	166

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (iii) $-x, y, -z+1/2$; (v) $x+1, -y+1, z+1/2$; (vi) $-x, -y+1, -z+1$; (vii) $-x+1, -y+2, -z+1$; (viii) $x, -y+2, z+1/2$; (ix) $x, y+1, z$.