



Three new acid M^+ arsenates and phosphates with multiply protonated As/ PO_4 groups

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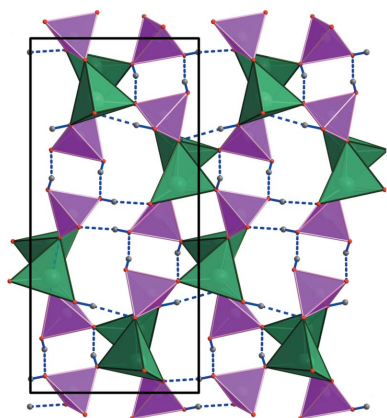
The crystal structures of caesium dihydrogen arsenate(V) bis[trihydrogen arsenate(V)], $Cs(H_2AsO_4)(H_3AsO_4)_2$, ammonium dihydrogen arsenate(V) trihydrogen arsenate(V), $NH_4(H_2AsO_4)(H_3AsO_4)$, and dilithium bis(dihydrogen phosphate), $Li_2(H_2PO_4)_2$, were solved from single-crystal X-ray diffraction data. $NH_4(H_2AsO_4)(H_3AsO_4)$, which was hydrothermally synthesized ($T = 493$ K), is homeotypic with $Rb(H_2AsO_4)(H_3AsO_4)$, while $Cs(H_2AsO_4)(H_3AsO_4)_2$ crystallizes in a novel structure type and $Li_2(H_2PO_4)_2$ represents a new polymorph of this composition. The Cs and Li compounds grew at room temperature from highly acidic aqueous solutions. $Li_2(H_2PO_4)_2$ forms a three-dimensional (3D) framework of PO_4 tetrahedra sharing corners with Li_2O_6 dimers built of edge-sharing LiO_4 groups, which is reinforced by hydrogen bonds. The two arsenate compounds are characterized by a 3D network of AsO_4 groups that are connected solely *via* multiple strong hydrogen bonds. A statistical evaluation of the As—O bond lengths in singly, doubly and triply protonated AsO_4 groups gave average values of 1.70 (2) Å for 199 As—OH bonds, 1.728 (19) Å for As—OH bonds in $HAsO_4$ groups, 1.714 (12) Å for As—OH bonds in H_2AsO_4 groups and 1.694 (16) Å for As—OH bonds in H_3AsO_4 groups, and a grand mean value of 1.667 (18) Å for As—O bonds to nonprotonated O atoms.

1. Introduction

M^+ phosphates and arsenates, and their crystal structures and physicochemical properties, have been extensively studied. Several compounds exhibit interesting properties, such as protonic conductivity (Chouchene *et al.*, 2017*a,b*; Volkov *et al.*, 1995, 1997; Voronov *et al.*, 2013; Dekhili *et al.*, 2018) or nonlinear optical properties (Dhouib *et al.*, 2014*a*, 2017; Kumaresan *et al.*, 2008).

To further increase the knowledge about the possible compounds and structure types of M^+M^{3+} arsenates, a comprehensive study of the system $M^+M^{3+}O-(H-)As/P^{5+}$ ($M^+ = Li, Na, K, Rb, Cs, Ag, Tl$ and NH_4 ; $M^{3+} = Al, Ga, In, Sc, Fe, Cr$ and Tl) was undertaken, which led to a large number of new structure types that have been published (Schwendtner, 2006; Schwendtner & Kolitsch, 2004*a,b*, 2005, 2007*a,b,c*, 2017*a,b*, 2018). The three compounds structurally characterized in the present article are by-products of this comprehensive study. The following paragraphs provide brief backgrounds to the families of materials to which the three compounds belong.

Lithium phosphates are rather common and the system Li—H—P—O has been widely studied because of the proton conductivity of compounds like LiH_2PO_4 (Catti & Ivaldi, 1978). The title compound $Li_2(H_2PO_4)_2$ is a new polymorph of



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Table 1
Experimental details.

Experiments were carried out at 293 K with Mo $K\alpha$ radiation using a Nonius KappaCCD single-crystal four-circle diffractometer. Absorption was corrected for by multi-scan methods (SCALEPACK; Otwinowski *et al.*, 2003).

	Cs(H₂AsO₄)(H₃AsO₄)₂	(NH₄)(H₂AsO₄)(H₃AsO₄)	Li₂(H₂PO₄)₂
Crystal data			
Chemical formula	Cs(H ₂ AsO ₄)(H ₃ AsO ₄) ₂	(NH ₄)(H ₂ AsO ₄)(H ₃ AsO ₄)	Li ₂ (H ₂ PO ₄) ₂
M_r	557.73	300.92	207.85
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/n$
a, b, c (Å)	9.712 (2), 12.738 (3), 9.307 (2)	7.943 (2), 9.855 (2), 19.623 (4)	5.400 (1), 15.927 (3), 7.562 (2)
α, β, γ (°)	90, 90.91 (3), 90	90, 90, 90	90, 90.47 (3), 90
V (Å ³)	1151.2 (4)	1536.1 (6)	650.4 (2)
Z	4	8	4
μ (mm ⁻¹)	11.83	8.71	0.67
Crystal size (mm)	0.14 × 0.13 × 0.08	0.15 × 0.10 × 0.07	0.15 × 0.12 × 0.10
Data collection			
T_{\min} , T_{\max}	0.288, 0.451	0.355, 0.581	0.906, 0.936
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8200, 4186, 3411	1799, 1295, 905	5625, 2857, 2490
Completeness to 0.84 Å resolution	1.00	0.65	1.00
R_{int}	0.016	0.038	0.014
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.758	0.676	0.806
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.054, 1.05	0.046, 0.109, 1.02	0.025, 0.072, 1.04
No. of reflections	4186	1295	2857
No. of parameters	178	136	126
No. of restraints	1	9	0
H-atom treatment	All H-atom parameters refined	Only H-atom coordinates refined	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.91, -1.60	0.74, -0.61	0.44, -0.38

Computer programs: COLLECT (Nonius, 2003), DENZO and SCALEPACK (Otwinowski *et al.*, 2003), SHELXS97 (Sheldrick, 2008), SHELXL2016 (Sheldrick, 2015), DIAMOND (Brandenburg, 2005) and publCIF (Westrip, 2010).

this well-known compound. Other known compounds in the Li–H–P–O system, the majority containing polymerized phosphate groups, include Li₄H(PO₃)₅, LiH₂PO₂, Li₆(P₆O₁₈)(H₂O)₃, Li₄P₂O₈(H₂O)₄, Li₃(P₃O₉)(H₂O)₃, Li₆(P₆O₁₈)(H₂O)₅, Li₄(P₄O₁₂)(H₂O)₅, Li₆(P₆O₁₈)(H₂O)_{8.24}, Li₆(P₆O₁₈)(H₂O)_{9.86}, Li₃PO₄ and Li₄P₂O₇.

Known caesium arsenates include CsAs₃O₈ (Schwendtner & Kolitsch, 2007a), Cs₃AsO₄ (Emmerling *et al.*, 2002), Cs₂(HAsO₄)(H₂O)₂ (Stöger & Weil, 2014), KDP-type Cs(H₂AsO₄) (Ferrari *et al.*, 1956) and CsH₅(AsO₄)₂ (Naili *et al.*, 2001). Ammonium arsenate compounds comprise (NH₄)(H₂AsO₄), for which a tetragonal KDP-type polymorph (Khan & Baur, 1972) and an orthorhombic low-temperature polymorph (Fukami, 1989) were reported, (NH₄)₂(HAsO₄) (Weil, 2012) and (NH₄)₃(AsO₄)(H₂O)₃ (Hseu & Lu, 1977).

Compounds containing H₃AsO₄ groups are relatively rare and mainly known from compounds containing organic groups (*e.g.* Dekola *et al.*, 2011; Dhoubib *et al.*, 2014a,b, 2017; Ratajczak *et al.*, 2000). Inorganic compounds containing arsenic acid (with clearly located H atoms of the H₃AsO₄ group) and with known crystal structures are restricted to only seven representatives: CuH₁₀(AsO₄)₄ (Tran Qui & Chiadmi, 1986) and isotypic ZnH₁₀(AsO₄)₄ (Sure & Guse, 1989) (the O–H bonds were not clearly identified in the latter structure determination), RbH₅(AsO₄)₂ (Naili & Mhiri, 2001), CsH₅(AsO₄)₂ (Naili *et al.*, 2001), K₄(SO₄)(HSO₄)₂(H₃AsO₄) (Amri *et al.*, 2007), Cs₄(SeO₄)(HSeO₄)₂(H₃AsO₄) (Amri *et al.*, 2009) and isotypic Rb₄(SO₄)(HSO₄)₂(H₃AsO₄) (Belhaj Salah *et al.*, 2018). (NH₄)₂(H₃AsO₄)(SO₄) (Boubia *et al.*, 1985) also con-

tains H₃AsO₄ groups, but the H atoms were not located, and for CdH₁₀(AsO₄)₄ (Tran Qui & Chiadmi, 1986), hydrogen-bond details were published, but no atomic coordinates.

2. Experimental

2.1. Synthesis and crystallization

Analytical grade chemicals were used for all syntheses. NH₄(H₂AsO₄)(H₃AsO₄) was grown by hydrothermal methods ($T = 493$ K, 7 d, Teflon-lined stainless steel autoclave) from a mixture of In₂O₃ and H₃AsO₄·0.5H₂O in an approximate volume ratio of 1:10 and 10 drops of NH₄(OH) (32%). No additional H₂O was added. The reaction product was a solid mass of colourless intergrown crystals with less than 10 vol% of a yellow unidentified material. The NH₄(H₂AsO₄)(H₃AsO₄) crystals are stable in air.

Cs(H₂AsO₄)(H₃AsO₄)₂ formed as the secondary product from further reaction of hydrothermally grown CsAs₃O₈ (Schwendtner & Kolitsch, 2007a). CsAs₃O₈ contains AsO₆ groups, is highly hygroscopic and, at room temperature, decomposes to a highly acidic liquid in which rounded prismatic glassy colourless crystals of Cs(H₂AsO₄)(H₃AsO₄)₂ grew within a few weeks.

Li₂(H₂PO₄)₂ was also a secondary product of a hydrothermal run ($T = 493$ K, 7 d, Teflon-lined stainless steel autoclave) from a mixture of Li₂CO₃, Ga₂O₃, phosphoric acid and distilled water. The initial and final pH values were both about 1. The hydrothermal synthesis yielded globular crystal

Table 2
Selected bond lengths (Å) for Cs(H₂AsO₄)(H₃AsO₄)₂.

Cs1—O6 ⁱ	3.1202 (17)	As1—O1	1.6437 (15)
Cs1—O2 ⁱⁱ	3.2184 (19)	As1—O2	1.6903 (17)
Cs1—O3 ⁱⁱⁱ	3.2326 (19)	As1—O3	1.6970 (17)
Cs1—O4	3.2469 (17)	As1—O4	1.7025 (16)
Cs1—O5 ^{iv}	3.2536 (18)	As2—O5	1.6390 (16)
Cs1—O1 ^v	3.3579 (17)	As2—O6	1.6874 (16)
Cs1—O11 ^{vi}	3.359 (2)	As2—O7	1.6977 (19)
Cs1—O12	3.478 (2)	As2—O8	1.7004 (19)
Cs1—O9 ^{vii}	3.7056 (19)	As3—O9	1.6515 (16)
Cs1—O11 ^{viii}	3.755 (3)	As3—O10	1.6579 (17)
Cs1—O8	3.844 (2)	As3—O12	1.707 (2)
Cs1—O7 ^{vii}	3.924 (3)	As3—O11	1.7104 (19)

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

aggregates of rounded hexagonal prisms of GaPO₄. From the remaining acidic liquid of the synthesis, Li₂(H₂PO₄)₂ grew as colourless crude block-shaped crystals by slow evaporation at room temperature.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. NH₄(H₂AsO₄)(H₃AsO₄) disintegrated ('melted') during the measurement, so only the first two sets or 65% of the Ewald sphere could be measured. Specifically, we note that out of the nine sets collected, the first two were fully usable (no decay visible); the decay only started with set 3, so we ignored sets 3–9. We did not observe any anomalous behaviour of the data set during scaling. The remaining sets showed a pseudocubic *I*-centred tetragonal unit cell, with approximate *a* and *c* values of 7.68 and 7.69 Å, respectively; possibly NH₄(H₂AsO₄)(H₃AsO₄) recrystallized to pseudocubic $\bar{I}42d$ -type (NH₄)₂H₂AsO₄ (Fukami, 1989). Nine reflections with negative intensities (blocked by the beam stop) were omitted from the refinement. All N–H and O–H bonds were restricted to 0.9 ± 0.2 Å, as was the O6–H6 bond in Cs(H₂AsO₄)(H₃AsO₄)₂. The O–H bonds in Li₂(H₂PO₄)₂

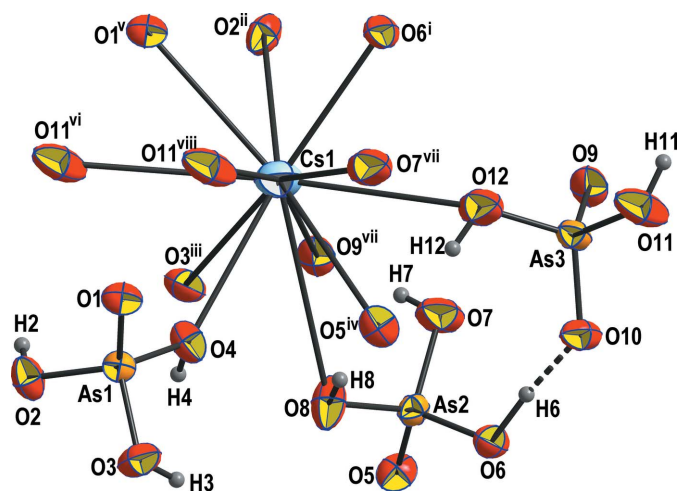


Figure 1
The principal building unit of Cs(H₂AsO₄)(H₃AsO₄)₂, shown as displacement ellipsoids at the 70% probability level. The symmetry codes are as defined in Table 2.

were not restrained as they refined to reasonable values for refinements based on the X-ray diffraction data sets.

3. Results and discussion

The asymmetric unit of Cs(H₂AsO₄)(H₃AsO₄)₂ contains one Cs, three As, 12 O and eight H atoms (Fig. 1). The Cs atom is 12-coordinated, with the Cs–O bond lengths varying between 3.1202 (17) and 3.934 (3) Å (Table 2). The average Cs–O bond length (3.458 Å) is considerably longer than the statistical average of 3.377 Å for 12-coordinated Cs atoms (Gagné & Hawthorne, 2016), explaining the low bond-valence sum (BVS; Gagné & Hawthorne, 2015) of 0.85 v.u. The As–O bond lengths are very similar for the doubly (As3) and triply protonated (As1 and As2) As atoms (1.683–1.681 Å) and slightly shorter than the statistical average of 1.687 Å (Gagné & Hawthorne, 2018a). Since two/three O atoms of the coordination polyhedra are protonated, the As–O bond lengths are only slightly elongated compared to unprotonated O atoms. The BVSs of the three As atoms are between 5.06 and 5.09 v.u. and thus close to the expected value, whereas all O atoms are considerably underbonded, with BVSs ranging from 1.22 to 1.53 v.u., and are all either donors or acceptors of hydrogen bonds. The latter are strong (compared to the other H₃AsO₄-containing compounds cited above), with O–H...O distances in the range 2.524 (2)–2.664 (2) Å (Table 3) and connect the individual protonated AsO₄ tetrahedra into a three-dimensional (3D) network (Figs. 2a–c). In the [101]

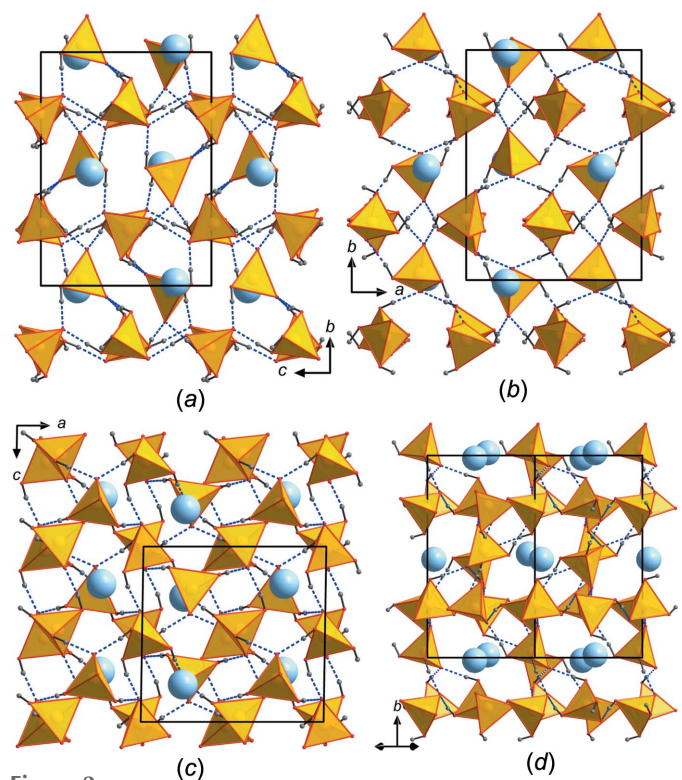


Figure 2
Structural drawings of novel Cs(H₂AsO₄)(H₃AsO₄)₂, viewed along (a) *a*, (b) *c*, (c) *b* and (d) [101]. The unit cell is outlined. AsO₄ tetrahedra (yellow) are connected *via* multiple hydrogen bonds (blue) into a 3D network. The Cs⁺ cations lie between the AsO₄ tetrahedra.

Table 3
 Hydrogen-bond geometry (Å, °) for Cs(H₂AsO₄)(H₃AsO₄)₂.

<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>
O2—H2···O10 ^{viii}	0.83 (4)	1.70 (4)	2.524 (2)	171 (4)
O3—H3···O9 ^{ix}	0.79 (4)	1.76 (4)	2.553 (3)	172 (4)
O4—H4···O1 ⁱⁱⁱ	0.92 (3)	1.70 (3)	2.609 (2)	170 (3)
O6—H6···O10	0.91 (2)	1.64 (2)	2.539 (2)	170 (4)
O7—H7···O9 ^{vii}	0.81 (4)	1.79 (4)	2.599 (3)	177 (4)
O11—H11···O1 ^{vi}	0.79 (4)	1.85 (4)	2.630 (3)	168 (4)
O8—H8···O5 ^{iv}	0.82 (4)	1.85 (4)	2.664 (2)	170 (4)
O12—H12···O5 ^{iv}	0.81 (4)	1.84 (4)	2.643 (3)	171 (4)

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

Table 4
 Selected bond lengths (Å) for (NH₄)(H₂AsO₄)(H₃AsO₄).

N—O5	2.869 (10)	N—O3 ⁱ	3.283 (10)
N—O1 ⁱ	2.947 (9)	As1—O1	1.648 (5)
N—O5 ⁱ	3.032 (11)	As1—O2	1.662 (6)
N—O2 ⁱⁱ	3.075 (9)	As1—O3	1.705 (6)
N—O4 ⁱⁱⁱ	3.082 (9)	As1—O4	1.714 (5)
N—O6	3.148 (10)	As2—O5	1.632 (6)
N—O7 ^{iv}	3.194 (10)	As2—O8	1.692 (5)
N—O3	3.216 (10)	As2—O7	1.693 (5)
N—O8 ^v	3.272 (9)	As2—O6	1.696 (6)

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

direction, the structure forms tunnels walled by AsO₄ tetrahedra in which the Cs atom is located (Fig. 2*d*).

The structure of (NH₄)(H₂AsO₄)(H₃AsO₄) is homeotypic with that of Rb(H₂AsO₄)(H₃AsO₄) (Naili & Mhiri, 2001); the Rb⁺ cation is replaced by an NH₄⁺ group providing additional hydrogen bonds to the atomic arrangement. This structure type is also closely related to that of CsH₅(AsO₄)₂ (Naili *et al.*, 2001), which can be seen as a distorted version of the Rb(H₂AsO₄)(H₃AsO₄) structure type. The structure of (NH₄)(H₂AsO₄)(H₃AsO₄) is built of individual, doubly or triply protonated AsO₄ tetrahedra that are connected *via* strong hydrogen bonds into a 3D network (Figs. 3, 4*a* and 4*b*). The NH₄⁺ groups lie in voids and further reinforce the network *via* medium-to-weak strength hydrogen bonds. AsO₄ tetrahedra and NH₄⁺ cations are arranged in layers perpendicular to *c* (Fig. 4). The NH₄⁺ cation is ten-coordinated, with an average N—O bond distance of 3.112 Å (Table 4), leading to a BVS of 0.97 v.u. (García-Rodríguez *et al.*, 2000). Both AsO₄ groups are overbonded (5.08 and 5.13 v.u. for As1 and

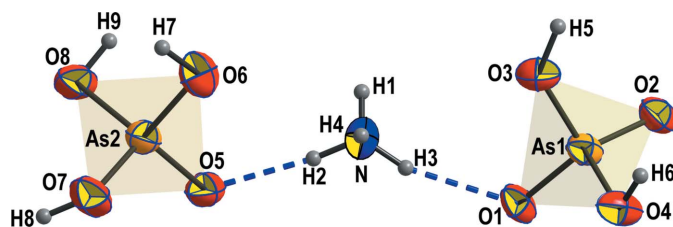


Figure 3
 The principal building unit of (NH₄)(H₂AsO₄)(H₃AsO₄), shown as displacement ellipsoids at the 70% probability level. Hydrogen bonds are shown as blue dashed lines.

Table 5
 Hydrogen-bond geometry (Å, °) for (NH₄)(H₂AsO₄)(H₃AsO₄).

<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>
N—H1···O4 ⁱⁱⁱ	0.89 (2)	2.36 (8)	3.082 (9)	138 (10)
N—H1···O7 ^{iv}	0.89 (2)	2.54 (9)	3.194 (10)	130 (9)
N—H4···O5 ⁱ	0.90 (2)	2.20 (7)	3.032 (11)	154 (14)
N—H3···O1 ⁱ	0.89 (2)	2.10 (4)	2.947 (9)	159 (9)
N—H2···O5	0.91 (2)	1.96 (2)	2.869 (10)	174 (7)
O3—H5···O1 ^{vi}	0.89 (2)	2.13 (15)	2.616 (7)	113 (12)
O3—H5···O3 ⁱⁱ	0.89 (2)	2.61 (11)	3.311 (12)	136 (13)
O6—H7···O2 ^{vii}	0.90 (2)	1.82 (10)	2.653 (9)	152 (19)
O4—H6···O1 ⁱ	0.89 (2)	1.77 (3)	2.650 (8)	170 (7)
O7—H8···O2 ^{viii}	0.89 (2)	1.72 (4)	2.568 (8)	157 (8)
O8—H9···O5 ^{iv}	0.89 (2)	1.78 (6)	2.590 (7)	150 (11)

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

As2, respectively), although the average As—O bond lengths (1.682 and 1.678 Å) are fairly close to the statistical average of 1.687 Å (Gagné & Hawthorne, 2018*a*). All O atoms are considerably underbonded and participate in a complex hydrogen-bonding network (Table 5). In Rb(H₂AsO₄)(H₃AsO₄) (Naili & Mhiri, 2001), there are some very strong hydrogen bonds present (2.432 Å) that connect the structure along the *c* axis. Hydrogen bonds with O—H···O distances < 2.5 Å are also present in many isostructural *M*⁺H₅(PO₄)₂ compounds [see compilation in Naili & Mhiri (2001)]. In (NH₄)(H₂AsO₄)(H₃AsO₄), these O—H···O hydrogen bonds are still strong but considerably longer, ranging from 2.568 (8) to 2.653 (9) Å. This is probably due to a small shift of the atom positions in the two compounds, seen also from an inspection of the unit cells of the two homeotypic compounds. While unit-cell parameters *a* and *b* are quite similar and 0.003 and 0.033 Å longer, respectively, in the ammonium compound, unit-cell

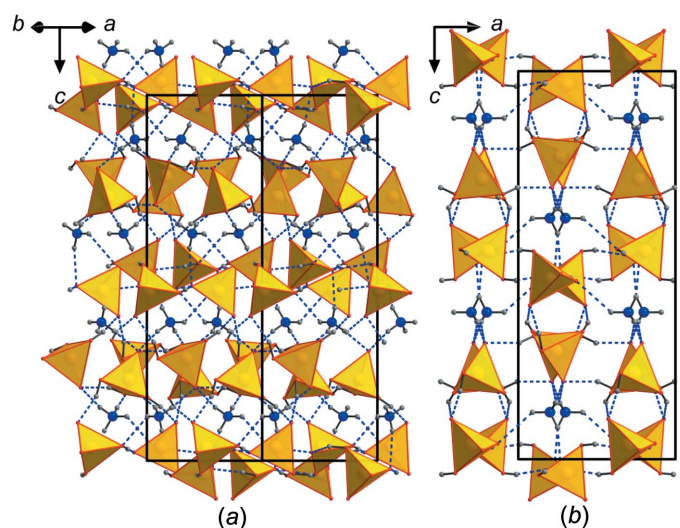


Figure 4
 Structural drawings of (NH₄)(H₂AsO₄)(H₃AsO₄), viewed along (a) [110] and (b) *b*. The unit cell is outlined. AsO₄ tetrahedra (yellow) are connected *via* multiple hydrogen bonds (blue dashed lines) into a 3D network. AsO₄ tetrahedra and NH₄⁺ cations are arranged in layers perpendicular to *c*. Additional hydrogen bonds of medium strength are provided by the NH₄⁺ cations.

Table 6
Hydrogen-bond geometry (Å, °) for $\text{Li}_2(\text{H}_2\text{PO}_4)_2$.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O}3-\text{H}1\cdots\text{O}7^{\text{vi}}$	0.77 (2)	1.91 (2)	2.6769 (12)	171 (2)
$\text{O}4-\text{H}2\cdots\text{O}2^{\text{iv}}$	0.84 (2)	1.99 (2)	2.8292 (14)	176 (2)
$\text{O}7-\text{H}3\cdots\text{O}6^{\text{vii}}$	0.73 (2)	1.79 (2)	2.5210 (13)	172 (3)
$\text{O}8-\text{H}4\cdots\text{O}1^{\text{viii}}$	0.79 (2)	1.79 (2)	2.5667 (12)	167 (2)

Symmetry codes: (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + 2, -y + 1, -z + 1$; (viii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 7
Selected bond lengths (Å) for $\text{Li}_2(\text{H}_2\text{PO}_4)_2$.

$\text{Li}1-\text{O}5$	1.888 (2)	$\text{Li}2-\text{P}2^{\text{iv}}$	3.077 (2)
$\text{Li}1-\text{O}6^{\text{i}}$	1.902 (2)	$\text{P}1-\text{O}1$	1.4996 (9)
$\text{Li}1-\text{O}8^{\text{ii}}$	1.967 (2)	$\text{P}1-\text{O}2$	1.5043 (8)
$\text{Li}1-\text{O}2$	2.045 (2)	$\text{P}1-\text{O}3$	1.5588 (9)
$\text{Li}1-\text{Li}2^{\text{iii}}$	2.611 (3)	$\text{P}1-\text{O}4$	1.5917 (8)
$\text{Li}1-\text{P}2^{\text{i}}$	3.068 (2)	$\text{P}2-\text{O}5$	1.4944 (8)
$\text{Li}2-\text{O}5^{\text{iv}}$	1.919 (2)	$\text{P}2-\text{O}6$	1.5113 (8)
$\text{Li}2-\text{O}1$	1.944 (2)	$\text{P}2-\text{O}7$	1.5640 (9)
$\text{Li}2-\text{O}4^{\text{v}}$	1.973 (2)	$\text{P}2-\text{O}8$	1.5774 (8)
$\text{Li}2-\text{O}2^{\text{iv}}$	1.974 (2)		

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

parameter c is considerably shorter [19.623 (4) Å; Table 1] in comparison with that of the rubidium compound [20.4226 (6) Å; Naili & Mhiri, 2001], leading also to a distinctly smaller unit-cell volume of $(\text{NH}_4)(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$. This change is explained, unlike what is expected from the slightly different effective ionic radii of NH_4^+ and Rb^+ (the latter is slightly smaller), firstly, by the ability of the NH_4^+ cation to form hydrogen bonds, and, secondly, by a slight shift of the $\text{As}1$ atoms in the b direction and a slight expansion in that direction. Hydrogen bonds connecting adjacent $\text{As}2\text{O}_4$ tetrahedra in the b direction in $\text{Rb}(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$ are lost and replaced by hydrogen bonds connecting $\text{As}1\text{O}_4$ and $\text{As}2\text{O}_4$ along c in $(\text{NH}_4)(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$ (Fig. 5), resulting in a compression of the whole structure along c .

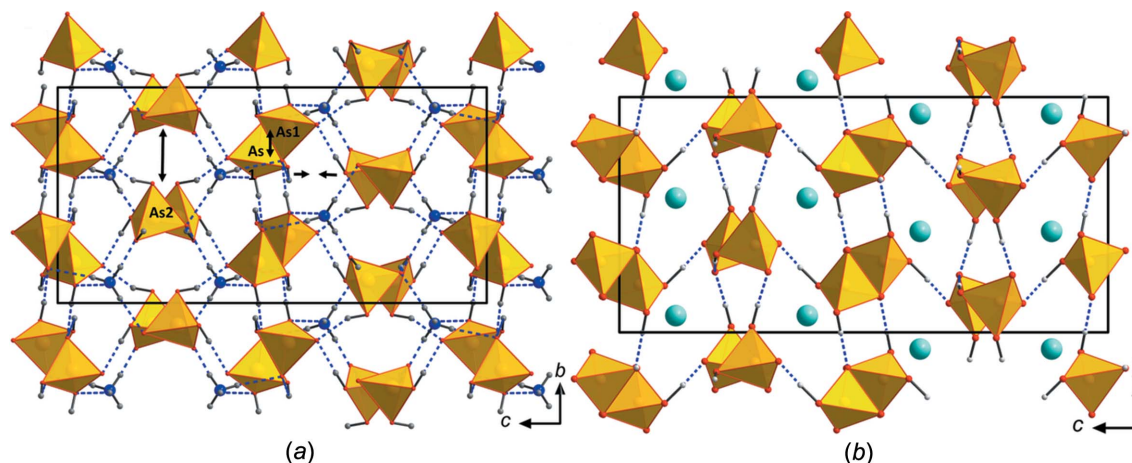


Figure 5
Comparison of (a) homeotypic $(\text{NH}_4)(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$ with (b) $\text{Rb}(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$ (Naili & Mhiri, 2001). A shift (arrows in figure) of $\text{As}1$ in the b direction leads to a compression of the whole structure along c , and results in a change of the hydrogen-bonding network. Hydrogen bonds connecting $\text{As}2\text{O}_4$ tetrahedra along b are lost in $(\text{NH}_4)(\text{H}_2\text{AsO}_4)(\text{H}_3\text{AsO}_4)$, but new hydrogen bonds now connect $\text{As}1\text{O}_4$ and $\text{As}2\text{O}_4$ along c .

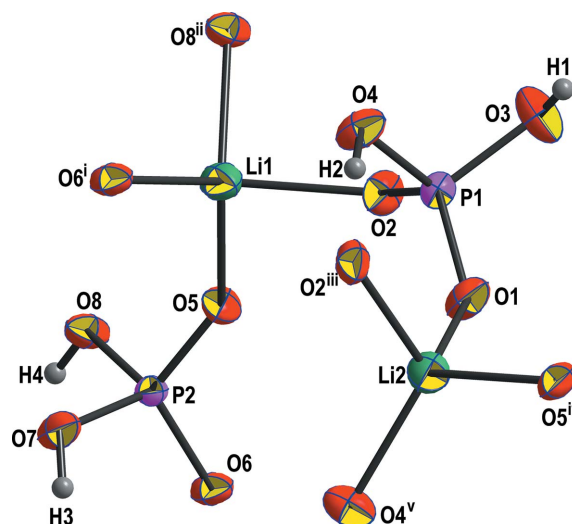


Figure 6
The principal building unit of $\text{Li}_2(\text{H}_2\text{PO}_4)_2$, shown with displacement ellipsoids at the 70% probability level. The symmetry codes are as defined in Table 7.

The asymmetric unit of monoclinic ($P2_1/n$) $\text{Li}_2(\text{H}_2\text{PO}_4)_2$ contains two Li, two P, eight O and four H atoms, all in general positions (Fig. 6). $\text{Li}_2(\text{H}_2\text{PO}_4)_2$ is built of LiO_4 tetrahedra that share edges with adjacent LiO_4 tetrahedra, thereby forming Li_2O_6 dimers (Fig. 7b). Each corner of the LiO_4 tetrahedra shares a corner with a PO_4 tetrahedron, thus connecting the Li_2O_6 dimers into a 3D network (Figs. 7a and 7b). This network is reinforced by hydrogen bonds of medium-to-high strength (Table 6). In the orthorhombic ($Pna2_1$) dimorph of $\text{Li}(\text{H}_2\text{PO}_4)$ (Catti & Ivaldi, 1978), which is characterized by a high electrical (proton) conductivity (Hwan Oh *et al.*, 2010), the LiO_4 tetrahedra share corners, thus forming chains that are connected by the PO_4 groups. In monoclinic $\text{Li}_2(\text{H}_2\text{PO}_4)_2$, the average (Table 7) $\text{Li}-\text{O}$ (1.951 and 1.953 Å) and $\text{P}-\text{O}$ (1.539 and 1.537 Å) bond lengths are very close to the statistical average of 1.972 Å (Gagné & Hawthorne, 2016) for $\text{Li}-\text{O}$ and 1.537 Å (Gagné & Hawthorne, 2018b) for $\text{P}-\text{O}$.

Table 8

Statistical analysis of the As—O bond lengths (Å) in H_nAsO_4 ($n = 1-3$) groups.

Bond lengths	Analysed number	Average	Minimum	Maximum
As—O/OH in H_nAsO_4 (average)	97	1.687 (6)	1.660	1.709
As—O/OH in H_nAsO_4 (individual)	388	1.687 (27)	1.614	1.801
As—OH in H_nAsO_4 (including split H-atom positions)	199	1.701 (23)	1.625	1.801
As—OH in H_nAsO_4 (no split H atoms)	117	1.714 (21)	1.625	1.801
As—OH in $HAsO_4$	43	1.728 (19)	1.689	1.801
As—OH in H_2AsO_4	41	1.714 (12)	1.688	1.749
As—OH in H_3AsO_4	33	1.694 (16)	1.625	1.712
As—OH/2 (split H atoms) in $H_{1-2}AsO_4$	82	1.683 (13)	1.656	1.714
As—O (no H atoms) in H_nAsO_4	189	1.671 (23)	1.614	1.755
As—O (no H/As*) in H_nAsO_4	174	1.667 (18)	1.614	1.735

Note: (*) no As—O—As bonds (see text).

bond lengths. This is also reflected by the nearly ideal BVSS (Gagné & Hawthorne, 2015) of 1.01 and 1.00 v.u. for Li1 and Li2, respectively, and 4.98 and 5.00 v.u. for P1 and P2, respectively. The most underbonded O atoms (O3, O4, O7 and O8, with BVSSs of 1.16–1.37 v.u.) form strong-to-medium hydrogen bonds (Table 6). A comparison of the X-ray densities of monoclinic $Li_2(H_2PO_4)_2$ (2.123 kg m^{-3}) and its orthorhombic dimorph LiH_2PO_4 (Catti & Ivaldi, 1978) (2.09 kg m^{-3}) suggests that monoclinic $Li_2(H_2PO_4)_2$ is slightly denser and therefore thermodynamically slightly more stable, at least under ambient conditions. Orthorhombic LiH_2PO_4 shows no phase transition between room temperature and 100 (Hwan Oh *et al.*, 2010) or 17 K (Lee *et al.*, 2008). We note that monoclinic $Li_2(H_2PO_4)_2$ most probably has an isotopic arsenate analogue, since Remy & Bachet (1967) were able to synthesize monoclinic $Li_2(H_2AsO_4)_2$, with $a = 5.55$, $b = 16.36$, $c = 7.80 \text{ Å}$, $\beta = 90.53^\circ$ and space group $P2_1/n$, although they did not determine its crystal structure. Orthorhombic $Li(H_2PO_4)$ also has an isotopic arsenate analogue, the crystal structure of which was reported by Fanchon *et al.* (1987), who pointed out a slight rearrangement in one of the two independent hydrogen bonds.

4. Statistical evaluation of As—O bonds in protonated AsO_4 groups

Several statistical analyses of bond lengths in $As^{5+}O_4$ polyhedra have been published recently. Gagné & Hawthorne (2018a) reported average As—O bond lengths of 1.687 (27) Å in AsO_4 and 1.830 (28) Å in AsO_6 groups, derived from 508 and 13 polyhedra, respectively. Schwendtner (2008) found similar values of 1.686 (29) and 1.827 (29) Å for a larger sample size of 704 AsO_4 and 40 AsO_6 polyhedra, respectively. An analysis of As—O bond lengths in minerals by Majzlan *et al.* (2014) gave a very similar value of 1.685 Å (no s.u. given) for the average As—O bond length and a value of 1.727 Å (no s.u. given) for As—OH bonds. Data for As—O bond lengths in multiply protonated $As^{5+}O_x$ ($x = 4$ and 6) polyhedra are scarce (especially those for H_3AsO_4 groups) due to the rare occurrence of compounds containing such polyhedra. An earlier attempt by Ichikawa (1988) to carry out a statistical analysis of the hydrogen-bond-length dependence of the distortion in H_nAsO_4 ($n = 1-3$) tetrahedra was severely hampered for the

doubly and triply protonated representatives, since data for only six H_2AsO_4 and two H_3AsO_4 groups were available, and no pertinent conclusions were possible. As the number of synthetic compounds and minerals containing H_nAsO_4 ($n = 1-3$) groups has considerably increased in the last three decades, we were able to perform a detailed analysis of As—O/OH bonds in H_nAsO_4 ($n = 1-3$) groups using data from the ICSD database (FIZ, 2018) (conventional R value < 5, full occupancy of As and O sites), expanded by the published data for known H_3AsO_4 -containing inorganic compounds mentioned in the *Introduction* (§1), and the two novel title arsenate compounds (Table 8 and Fig. 8).

The average As—O/OH bond length for the 97 analysed H_nAsO_4 ($n = 1-3$) groups of 1.686 (27) Å is nearly identical to the value reported by Gagné & Hawthorne (2018a), but the individual bond lengths vary greatly with the number of As—OH bonds in the respective polyhedra. While the As—OH bonds are extremely elongated to 1.728 (19) Å in $HAsO_4$ groups and to 1.714 (12) Å in H_2AsO_4 groups, the average As—OH bond length is considerably shorter, with a value of 1.694 (16) Å in the rare H_3AsO_4 groups. This result is in agreement with the observation of Ferraris & Ivaldi (1984) that the average length of $X-OH$ ($X = As$ and P) bonds tends to decrease from mono- to triprotonated anions with the same

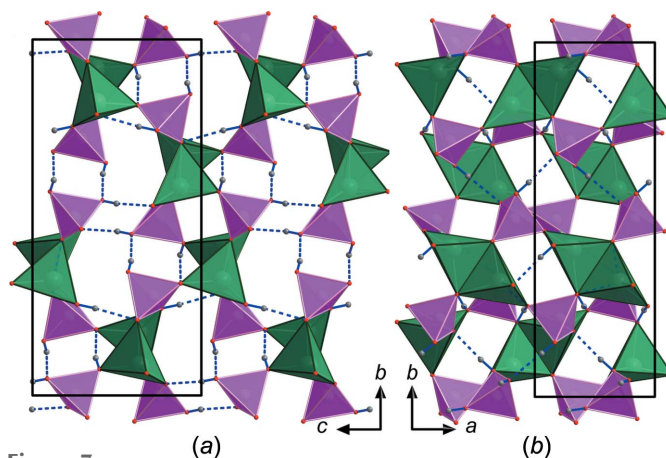
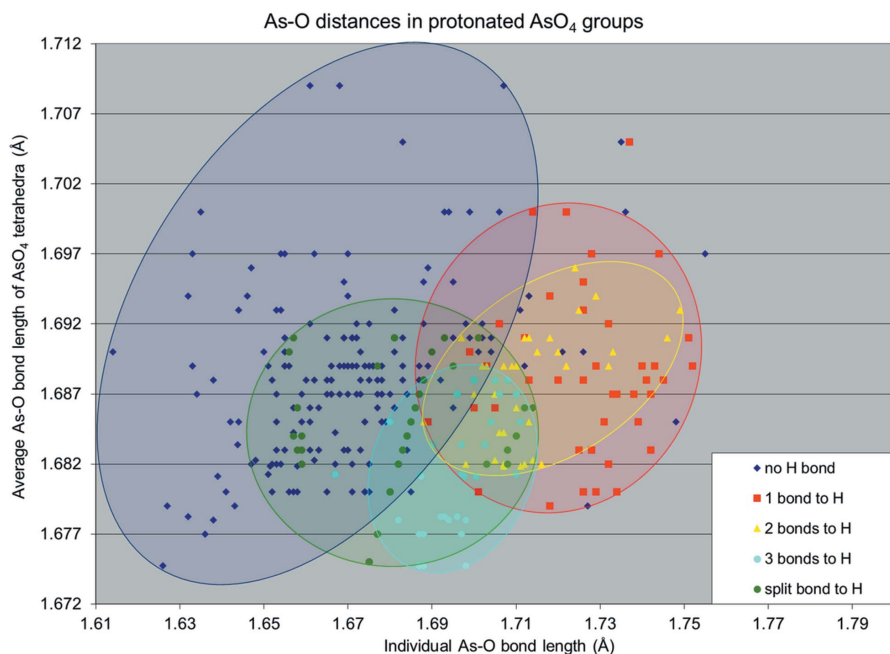


Figure 7
Structural drawings of $Li_2(H_2PO_4)_2$, viewed along (a) a and (b) c . The unit cell is outlined. Phosphate tetrahedra are shown in pink and edge-sharing LiO_4 tetrahedra in green. The hydrogen bonds reinforcing the network are shown in blue.


Figure 8

Comparison of As—O distances in H_nAsO_4 ($n = 1-3$) groups, sorted by As—OH bonds into clouds for H_3AsO_4 (turquoise), H_2AsO_4 (yellow) and $HAsO_4$ (red) groups. As—OH bonds to split H-atom positions are shown in green, while all bonds to the remaining nonprotonated O atoms are shown in blue.

X atom. We also find that the As bonds to nonprotonated O atoms in H_3AsO_4 groups are shortened to 1.671 (23) Å. If As—O bonds involving bridging O ligands (as present in the As_2O_7 groups in pyroarsenates), *i.e.* As—O—As bonds, are removed from the data set because they are known to be anomalously elongated due to As—As repulsion, the value is even shorter, *i.e.* 1.667 (18) Å. A special case are As—O bonds to half-occupied H-atom positions; these are actually shortened to 1.683 (13) Å. Excluding split H-atom positions, the grand mean average As—OH bond length in H_nAsO_4 ($n = 1-3$) groups is 1.714 (21) Å and thus considerably shorter than the value of 1.727 Å derived by Majzlan *et al.* (2014), whose evaluation was based mainly on $H_{1-2}AsO_4$ groups. A visual analysis of the individual As—O bond lengths compared to the averages of the H_nAsO_4 ($n = 1-3$) groups (Fig. 8) shows that they form clearly distributed clouds, depending on the number of H atoms. The average As—O/OH bond lengths of the polyhedra, as well as the individual As—OH bond lengths, are largest in $HAsO_4$ groups and show a narrower distribution in H_2AsO_4 . The population of H_3AsO_4 groups is characterized by shorter individual As—OH bond lengths but also a shorter average As—OH bond length of the polyhedra. It can also be recognized that the whole data set shows a strong concentration of bonds at around *ca* 1.687 Å and that all the shortest bonds are to the nonprotonated O atoms of each H_nAsO_4 ($n = 1-3$) group (blue cloud in Fig. 8, *cf.* Table 8). This is expected because the As atom in each H_nAsO_4 tries to achieve a BVS of 5, and due to the elongation of all the bonds to protonated O atoms, the remaining As—O bonds have to shorten accordingly. This also explains why both the individual As—OH bond lengths and average As—O(H) bond lengths decrease with increasing protonation. In the case of singly protonated

AsO_4 groups, the three As—O bonds need to become slightly shortened in order to still achieve a BVS of 5, at the expense of a high bond-length distortion in this tetrahedron. In agreement with the distortion theorem (Brown & Shannon, 1973), this results in a slightly higher value of the average As—O(H) bond length of 1.689 (6) Å in $HAsO_4$ groups (vertical range of red cloud in Fig. 8) *versus* a corresponding value of 1.688 (3) Å in H_2AsO_4 groups (vertical range of yellow cloud) and the notably lower value of 1.680 (7) Å in H_3AsO_4 groups (vertical range of turquoise cloud). This low value in the latter is a consequence of three competing As—OH bonds which can only be counteracted by one As—O bond. This leads to three similarly short As—OH bonds and one even shorter As—O bond, *i.e.* a small bond-length distortion.

The overall spread of values is a consequence of the variable strengths of the hydrogen bonds in the individual compounds. A conspicuous outlier in Fig. 8 (*e.g.* in the top-right corner) may be explained by the influence of a very strong hydrogen bond in $Mg(HAsO_4)(H_2O)_7$, with an O...O donor-acceptor distance of 2.491 Å (no s.u. given; Ferraris & Franchini-Angela, 1973).

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supporting information

Acta Cryst. (2019). C75, 1134-1141 [https://doi.org/10.1107/S2053229619008489]

Three new acid M^+ arsenates and phosphates with multiply protonated As/ PO_4 groups

Karolina Schwendtner and Uwe Kolitsch

Computing details

For all structures, data collection: *COLLECT* (Nonius, 2003); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO* and *SCALEPACK* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Caesium dihydrogen arsenate(V) bis[trihydrogen arsenate(V)] (CsH₂AsO₄H₃AsO₄)

Crystal data

Cs(H₂AsO₄)(H₃AsO₄)₂

$M_r = 557.73$

Monoclinic, $P2_1/c$

$a = 9.712$ (2) Å

$b = 12.738$ (3) Å

$c = 9.307$ (2) Å

$\beta = 90.91$ (3)°

$V = 1151.2$ (4) Å³

$Z = 4$

$F(000) = 1032$

$D_x = 3.218$ Mg m⁻³

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

Cell parameters from 4360 reflections

$\theta = 2.7$ – 32.6 °

$\mu = 11.83$ mm⁻¹

$T = 293$ K

Rounded prisms, colourless

$0.14 \times 0.13 \times 0.08$ mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan

(*SCALEPACK*; Otwinowski *et al.*, 2003)

$T_{\min} = 0.288$, $T_{\max} = 0.451$

8200 measured reflections

4186 independent reflections

3411 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 32.6$ °, $\theta_{\min} = 2.7$ °

$h = -14 \rightarrow 14$

$k = -19 \rightarrow 19$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.054$

$S = 1.05$

4186 reflections

178 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 1.0466P]$

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

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.91$ e Å⁻³

$\Delta\rho_{\min} = -1.60$ e Å⁻³

Extinction correction: SHELXL2016
(Sheldrick, 2015),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00340 (11)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.22962 (2)	0.51389 (2)	0.27149 (2)	0.03776 (6)
As1	0.00263 (2)	0.23648 (2)	0.48710 (2)	0.01694 (5)
As2	0.46332 (2)	0.24756 (2)	0.02338 (2)	0.01917 (6)
As3	0.73534 (2)	0.47250 (2)	0.25789 (2)	0.02105 (6)
O1	0.01202 (17)	0.31350 (12)	0.62862 (15)	0.0225 (3)
O2	−0.15805 (17)	0.21801 (14)	0.41934 (18)	0.0273 (3)
O3	0.0553 (2)	0.11305 (13)	0.5291 (2)	0.0298 (4)
O4	0.10335 (17)	0.28641 (13)	0.35555 (17)	0.0255 (3)
O5	0.42912 (18)	0.17618 (13)	−0.11930 (16)	0.0262 (3)
O6	0.60947 (17)	0.20728 (13)	0.10689 (19)	0.0277 (4)
O7	0.4908 (2)	0.37667 (14)	−0.0112 (2)	0.0411 (5)
O8	0.32988 (19)	0.23889 (17)	0.1389 (2)	0.0351 (4)
O9	0.73949 (17)	0.54949 (13)	0.11525 (18)	0.0284 (4)
O10	0.75902 (17)	0.34537 (13)	0.22914 (17)	0.0269 (4)
O11	0.8597 (2)	0.50491 (15)	0.3823 (2)	0.0405 (5)
O12	0.5816 (2)	0.49272 (15)	0.3400 (2)	0.0417 (5)
H2	−0.179 (4)	0.265 (3)	0.360 (4)	0.061 (12)*
H3	0.115 (4)	0.095 (3)	0.477 (4)	0.067 (12)*
H4	0.081 (4)	0.250 (3)	0.273 (4)	0.054 (10)*
H6	0.659 (4)	0.262 (2)	0.144 (4)	0.080 (14)*
H7	0.420 (4)	0.402 (3)	−0.044 (4)	0.059 (11)*
H8	0.353 (4)	0.262 (3)	0.218 (4)	0.060 (11)*
H11	0.888 (4)	0.563 (3)	0.378 (4)	0.076 (14)*
H12	0.543 (4)	0.437 (3)	0.350 (4)	0.062 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.04230 (11)	0.02498 (8)	0.04561 (11)	0.00032 (6)	−0.01130 (8)	−0.00318 (7)
As1	0.01957 (10)	0.01814 (10)	0.01307 (9)	−0.00029 (8)	−0.00091 (7)	−0.00053 (7)
As2	0.01818 (11)	0.01998 (10)	0.01925 (11)	0.00205 (8)	−0.00274 (8)	−0.00085 (8)
As3	0.02387 (11)	0.01600 (11)	0.02320 (11)	−0.00176 (8)	−0.00263 (8)	0.00363 (8)
O1	0.0306 (8)	0.0218 (7)	0.0152 (7)	−0.0005 (6)	−0.0010 (6)	−0.0031 (6)
O2	0.0224 (8)	0.0343 (9)	0.0251 (8)	−0.0062 (7)	−0.0048 (6)	0.0062 (7)
O3	0.0371 (10)	0.0213 (8)	0.0311 (9)	0.0077 (7)	0.0072 (8)	0.0037 (7)

O4	0.0271 (8)	0.0314 (8)	0.0179 (7)	-0.0088 (7)	0.0032 (6)	-0.0016 (6)
O5	0.0298 (9)	0.0305 (8)	0.0182 (7)	0.0036 (7)	-0.0013 (6)	-0.0046 (6)
O6	0.0231 (8)	0.0205 (8)	0.0392 (9)	0.0011 (6)	-0.0103 (7)	0.0019 (7)
O7	0.0416 (12)	0.0211 (8)	0.0601 (13)	0.0007 (8)	-0.0166 (10)	0.0085 (8)
O8	0.0244 (9)	0.0577 (13)	0.0233 (9)	0.0012 (8)	0.0031 (7)	-0.0088 (8)
O9	0.0260 (8)	0.0283 (8)	0.0308 (8)	-0.0016 (7)	0.0001 (7)	0.0126 (7)
O10	0.0316 (9)	0.0179 (7)	0.0307 (8)	0.0019 (6)	-0.0105 (7)	-0.0006 (6)
O11	0.0527 (13)	0.0260 (9)	0.0419 (11)	-0.0106 (9)	-0.0227 (9)	0.0034 (8)
O12	0.0441 (12)	0.0246 (9)	0.0570 (13)	0.0001 (8)	0.0238 (10)	0.0039 (9)

Geometric parameters (Å, °)

Cs1—O6 ⁱ	3.1202 (17)	Cs1—H3 ⁱⁱⁱ	3.25 (4)
Cs1—O2 ⁱⁱ	3.2184 (19)	Cs1—H6 ⁱ	3.43 (4)
Cs1—O3 ⁱⁱⁱ	3.2326 (19)	As1—O1	1.6437 (15)
Cs1—O4	3.2469 (17)	As1—O2	1.6903 (17)
Cs1—O5 ^{iv}	3.2536 (18)	As1—O3	1.6970 (17)
Cs1—O1 ^v	3.3579 (17)	As1—O4	1.7025 (16)
Cs1—O11 ^{vi}	3.359 (2)	As2—O5	1.6390 (16)
Cs1—O12	3.478 (2)	As2—O6	1.6874 (16)
Cs1—O9 ^{vii}	3.7056 (19)	As2—O7	1.6977 (19)
Cs1—O11 ^{viii}	3.755 (3)	As2—O8	1.7004 (19)
Cs1—O8	3.844 (2)	As3—O9	1.6515 (16)
Cs1—O7 ^{vii}	3.924 (3)	As3—O10	1.6579 (17)
Cs1—O12 ^{vi}	4.028 (3)	As3—O12	1.707 (2)
Cs1—O7	4.077 (3)	As3—O11	1.7104 (19)
Cs1—O3 ⁱⁱ	4.103 (2)	O2—H2	0.83 (4)
Cs1—O10 ⁱ	4.2239 (19)	O3—H3	0.79 (4)
Cs1—As1 ⁱⁱ	4.3298 (9)	O4—H4	0.92 (3)
Cs1—As3 ^{vi}	4.3913 (10)	O6—H6	0.910 (18)
Cs1—As1 ^v	4.5175 (9)	O7—H7	0.81 (4)
Cs1—O2 ^v	4.527 (2)	O8—H8	0.82 (4)
Cs1—H8	3.46 (4)	O11—H11	0.79 (4)
Cs1—H12	3.27 (4)	O12—H12	0.81 (4)
Cs1—H2 ⁱⁱ	3.45 (4)		
O6 ⁱ —Cs1—O2 ⁱⁱ	70.42 (5)	As1 ⁱⁱ —Cs1—H12	142.7 (7)
O6 ⁱ —Cs1—O3 ⁱⁱⁱ	154.40 (5)	As3 ^{vi} —Cs1—H12	74.4 (6)
O2 ⁱⁱ —Cs1—O3 ⁱⁱⁱ	85.00 (5)	As1 ^v —Cs1—H12	124.7 (6)
O6 ⁱ —Cs1—O4	143.71 (4)	O2 ^v —Cs1—H12	103.5 (6)
O2 ⁱⁱ —Cs1—O4	140.79 (5)	H8—Cs1—H12	55.5 (9)
O3 ⁱⁱⁱ —Cs1—O4	61.72 (4)	O6 ⁱ —Cs1—H2 ⁱⁱ	57.7 (6)
O6 ⁱ —Cs1—O5 ^{iv}	100.47 (5)	O2 ⁱⁱ —Cs1—H2 ⁱⁱ	13.8 (6)
O2 ⁱⁱ —Cs1—O5 ^{iv}	153.62 (4)	O3 ⁱⁱⁱ —Cs1—H2 ⁱⁱ	98.4 (6)
O3 ⁱⁱⁱ —Cs1—O5 ^{iv}	98.54 (5)	O4—Cs1—H2 ⁱⁱ	149.2 (7)
O4—Cs1—O5 ^{iv}	59.07 (4)	O5 ^{iv} —Cs1—H2 ⁱⁱ	151.5 (7)
O6 ⁱ —Cs1—O1 ^v	74.39 (4)	O1 ^v —Cs1—H2 ⁱⁱ	53.0 (7)
O2 ⁱⁱ —Cs1—O1 ^v	58.54 (4)	O11 ^{vi} —Cs1—H2 ⁱⁱ	111.7 (6)

O3 ⁱⁱⁱ —Cs1—O1 ^v	99.22 (5)	O12—Cs1—H2 ⁱⁱ	105.6 (7)
O4—Cs1—O1 ^v	104.44 (4)	O9 ^{vii} —Cs1—H2 ⁱⁱ	82.5 (6)
O5 ^{iv} —Cs1—O1 ^v	144.69 (4)	O11 ^{viii} —Cs1—H2 ⁱⁱ	89.7 (7)
O6 ⁱ —Cs1—O11 ^{vi}	81.01 (5)	O8—Cs1—H2 ⁱⁱ	139.8 (6)
O2 ⁱⁱ —Cs1—O11 ^{vi}	122.02 (5)	O7 ^{vii} —Cs1—H2 ⁱⁱ	63.1 (7)
O3 ⁱⁱⁱ —Cs1—O11 ^{vi}	119.57 (5)	O12 ^{vi} —Cs1—H2 ⁱⁱ	113.4 (6)
O4—Cs1—O11 ^{vi}	66.48 (4)	O7—Cs1—H2 ⁱⁱ	104.7 (6)
O5 ^{iv} —Cs1—O11 ^{vi}	78.98 (5)	O3 ⁱⁱ —Cs1—H2 ⁱⁱ	51.9 (6)
O1 ^v —Cs1—O11 ^{vi}	65.72 (5)	O10 ⁱ —Cs1—H2 ⁱⁱ	22.8 (6)
O6 ⁱ —Cs1—O12	60.63 (5)	As1 ⁱⁱ —Cs1—H2 ⁱⁱ	29.3 (6)
O2 ⁱⁱ —Cs1—O12	111.52 (5)	As3 ^{vi} —Cs1—H2 ⁱⁱ	109.0 (6)
O3 ⁱⁱⁱ —Cs1—O12	126.27 (5)	As1 ^v —Cs1—H2 ⁱⁱ	57.1 (6)
O4—Cs1—O12	105.10 (5)	O2 ^v —Cs1—H2 ⁱⁱ	60.4 (6)
O5 ^{iv} —Cs1—O12	46.08 (4)	H8—Cs1—H2 ⁱⁱ	148.5 (9)
O1 ^v —Cs1—O12	133.57 (4)	H12—Cs1—H2 ⁱⁱ	118.8 (9)
O11 ^{vi} —Cs1—O12	94.97 (6)	O6 ⁱ —Cs1—H3 ⁱⁱⁱ	143.7 (7)
O6 ⁱ —Cs1—O9 ^{vii}	118.46 (5)	O2 ⁱⁱ —Cs1—H3 ⁱⁱⁱ	79.2 (7)
O2 ⁱⁱ —Cs1—O9 ^{vii}	70.13 (4)	O3 ⁱⁱⁱ —Cs1—H3 ⁱⁱⁱ	14.1 (7)
O3 ⁱⁱⁱ —Cs1—O9 ^{vii}	42.49 (4)	O4—Cs1—H3 ⁱⁱⁱ	72.3 (7)
O4—Cs1—O9 ^{vii}	94.38 (4)	O5 ^{iv} —Cs1—H3 ⁱⁱⁱ	97.9 (7)
O5 ^{iv} —Cs1—O9 ^{vii}	94.84 (4)	O1 ^v —Cs1—H3 ⁱⁱⁱ	106.4 (7)
O1 ^v —Cs1—O9 ^{vii}	118.64 (4)	O11 ^{vi} —Cs1—H3 ⁱⁱⁱ	133.4 (7)
O11 ^{vi} —Cs1—O9 ^{vii}	160.46 (4)	O12—Cs1—H3 ⁱⁱⁱ	116.3 (7)
O12—Cs1—O9 ^{vii}	93.83 (5)	O9 ^{vii} —Cs1—H3 ⁱⁱⁱ	28.4 (7)
O6 ⁱ —Cs1—O11 ^{viii}	113.59 (5)	O11 ^{viii} —Cs1—H3 ⁱⁱⁱ	84.4 (7)
O2 ⁱⁱ —Cs1—O11 ^{viii}	88.68 (5)	O8—Cs1—H3 ⁱⁱⁱ	54.9 (7)
O3 ⁱⁱⁱ —Cs1—O11 ^{viii}	71.56 (5)	O7 ^{vii} —Cs1—H3 ⁱⁱⁱ	82.1 (7)
O4—Cs1—O11 ^{viii}	62.61 (4)	O12 ^{vi} —Cs1—H3 ⁱⁱⁱ	153.0 (7)
O5 ^{iv} —Cs1—O11 ^{viii}	117.33 (4)	O7—Cs1—H3 ⁱⁱⁱ	58.7 (7)
O1 ^v —Cs1—O11 ^{viii}	42.94 (4)	O3 ⁱⁱ —Cs1—H3 ⁱⁱⁱ	48.7 (7)
O11 ^{vi} —Cs1—O11 ^{viii}	58.10 (6)	O10 ⁱ —Cs1—H3 ⁱⁱⁱ	115.8 (7)
O12—Cs1—O11 ^{viii}	152.77 (5)	As1 ⁱⁱ —Cs1—H3 ⁱⁱⁱ	69.2 (7)
O9 ^{vii} —Cs1—O11 ^{viii}	110.65 (5)	As3 ^{vi} —Cs1—H3 ⁱⁱⁱ	151.3 (7)
O6 ⁱ —Cs1—O8	135.06 (4)	As1 ^v —Cs1—H3 ⁱⁱⁱ	123.6 (7)
O2 ⁱⁱ —Cs1—O8	127.77 (4)	O2 ^v —Cs1—H3 ⁱⁱⁱ	143.6 (7)
O3 ⁱⁱⁱ —Cs1—O8	56.82 (4)	H8—Cs1—H3 ⁱⁱⁱ	66.2 (9)
O4—Cs1—O8	50.42 (4)	H12—Cs1—H3 ⁱⁱⁱ	111.5 (9)
O5 ^{iv} —Cs1—O8	43.09 (4)	H2 ⁱⁱ —Cs1—H3 ⁱⁱⁱ	93.0 (9)
O1 ^v —Cs1—O8	150.13 (4)	O6 ⁱ —Cs1—H6 ⁱ	15.1 (4)
O11 ^{vi} —Cs1—O8	108.28 (5)	O2 ⁱⁱ —Cs1—H6 ⁱ	56.4 (5)
O12—Cs1—O8	74.64 (4)	O3 ⁱⁱⁱ —Cs1—H6 ⁱ	141.4 (5)
O9 ^{vii} —Cs1—O8	57.64 (4)	O4—Cs1—H6 ⁱ	152.5 (7)
O11 ^{viii} —Cs1—O8	107.98 (4)	O5 ^{iv} —Cs1—H6 ⁱ	115.4 (4)
O6 ⁱ —Cs1—O7 ^{vii}	66.17 (5)	O1 ^v —Cs1—H6 ⁱ	63.5 (6)
O2 ⁱⁱ —Cs1—O7 ^{vii}	61.16 (4)	O11 ^{vi} —Cs1—H6 ⁱ	86.1 (7)
O3 ⁱⁱⁱ —Cs1—O7 ^{vii}	96.12 (5)	O12—Cs1—H6 ⁱ	73.9 (5)
O4—Cs1—O7 ^{vii}	137.19 (4)	O9 ^{vii} —Cs1—H6 ⁱ	113.1 (7)
O5 ^{iv} —Cs1—O7 ^{vii}	92.45 (4)	O11 ^{viii} —Cs1—H6 ⁱ	105.4 (6)

O1 ^v —Cs1—O7 ^{vii}	115.59 (4)	O8—Cs1—H6 ⁱ	146.3 (6)
O11 ^{vi} —Cs1—O7 ^{vii}	144.05 (5)	O7 ^{vii} —Cs1—H6 ⁱ	66.0 (7)
O12—Cs1—O7 ^{vii}	56.84 (5)	O12 ^{vi} —Cs1—H6 ⁱ	71.1 (5)
O9 ^{vii} —Cs1—O7 ^{vii}	53.85 (4)	O7—Cs1—H6 ⁱ	110.1 (7)
O11 ^{viii} —Cs1—O7 ^{vii}	148.74 (4)	O3 ⁱⁱ —Cs1—H6 ⁱ	94.6 (4)
O8—Cs1—O7 ^{vii}	86.80 (4)	O10 ⁱ —Cs1—H6 ⁱ	21.7 (4)
O6 ⁱ —Cs1—O12 ^{vi}	58.18 (4)	As1 ⁱⁱ —Cs1—H6 ⁱ	71.6 (4)
O2 ⁱⁱ —Cs1—O12 ^{vi}	127.11 (4)	As3 ^{vi} —Cs1—H6 ⁱ	73.5 (6)
O3 ⁱⁱⁱ —Cs1—O12 ^{vi}	147.33 (4)	As1 ^v —Cs1—H6 ⁱ	52.9 (7)
O4—Cs1—O12 ^{vi}	86.18 (4)	O2 ^v —Cs1—H6 ⁱ	37.9 (7)
O5 ^{iv} —Cs1—O12 ^{vi}	56.21 (4)	H8—Cs1—H6 ⁱ	141.1 (8)
O1 ^v —Cs1—O12 ^{vi}	94.31 (4)	H12—Cs1—H6 ⁱ	86.2 (8)
O11 ^{vi} —Cs1—O12 ^{vi}	42.12 (5)	H2 ⁱⁱ —Cs1—H6 ⁱ	43.2 (8)
O12—Cs1—O12 ^{vi}	53.27 (6)	H3 ⁱⁱⁱ —Cs1—H6 ⁱ	133.6 (9)
O9 ^{vii} —Cs1—O12 ^{vi}	145.54 (4)	O1—As1—O2	114.91 (9)
O11 ^{viii} —Cs1—O12 ^{vi}	100.17 (5)	O1—As1—O3	110.85 (8)
O8—Cs1—O12 ^{vi}	98.93 (4)	O2—As1—O3	103.30 (9)
O7 ^{vii} —Cs1—O12 ^{vi}	104.61 (5)	O1—As1—O4	109.15 (8)
O6 ⁱ —Cs1—O7	105.03 (5)	O2—As1—O4	108.74 (8)
O2 ⁱⁱ —Cs1—O7	96.97 (4)	O3—As1—O4	109.70 (9)
O3 ⁱⁱⁱ —Cs1—O7	70.09 (5)	O1—As1—Cs1 ^{ix}	149.10 (6)
O4—Cs1—O7	90.81 (4)	O2—As1—Cs1 ^{ix}	39.80 (6)
O5 ^{iv} —Cs1—O7	60.59 (4)	O3—As1—Cs1 ^{ix}	70.95 (7)
O1 ^v —Cs1—O7	154.70 (4)	O4—As1—Cs1 ^{ix}	98.34 (6)
O11 ^{vi} —Cs1—O7	139.58 (5)	O1—As1—Cs1 ^v	37.17 (6)
O12—Cs1—O7	57.68 (5)	O2—As1—Cs1 ^v	79.53 (6)
O9 ^{vii} —Cs1—O7	38.65 (4)	O3—As1—Cs1 ^v	133.54 (6)
O11 ^{viii} —Cs1—O7	140.53 (4)	O4—As1—Cs1 ^v	113.07 (6)
O8—Cs1—O7	40.44 (4)	Cs1 ^{ix} —As1—Cs1 ^v	118.527 (15)
O7 ^{vii} —Cs1—O7	46.38 (5)	O1—As1—Cs1	82.60 (6)
O12 ^{vi} —Cs1—O7	106.93 (4)	O2—As1—Cs1	112.76 (6)
O6 ⁱ —Cs1—O3 ⁱⁱ	109.44 (4)	O3—As1—Cs1	131.43 (7)
O2 ⁱⁱ —Cs1—O3 ⁱⁱ	40.33 (4)	O4—As1—Cs1	28.57 (6)
O3 ⁱⁱⁱ —Cs1—O3 ⁱⁱ	48.55 (5)	Cs1 ^{ix} —As1—Cs1	120.358 (14)
O4—Cs1—O3 ⁱⁱ	100.71 (4)	Cs1 ^v —As1—Cs1	85.61 (2)
O5 ^{iv} —Cs1—O3 ⁱⁱ	146.51 (4)	O1—As1—Cs1 ^{iv}	86.21 (6)
O1 ^v —Cs1—O3 ⁱⁱ	61.34 (4)	O2—As1—Cs1 ^{iv}	122.72 (6)
O11 ^{vi} —Cs1—O3 ⁱⁱ	119.62 (5)	O3—As1—Cs1 ^{iv}	25.83 (6)
O12—Cs1—O3 ⁱⁱ	143.06 (5)	O4—As1—Cs1 ^{iv}	113.01 (6)
O9 ^{vii} —Cs1—O3 ⁱⁱ	57.92 (4)	Cs1 ^{ix} —As1—Cs1 ^{iv}	96.02 (2)
O11 ^{viii} —Cs1—O3 ⁱⁱ	63.81 (4)	Cs1 ^v —As1—Cs1 ^{iv}	115.679 (15)
O8—Cs1—O3 ⁱⁱ	103.48 (4)	Cs1—As1—Cs1 ^{iv}	122.793 (14)
O7 ^{vii} —Cs1—O3 ⁱⁱ	86.30 (4)	O5—As2—O6	111.26 (9)
O12 ^{vi} —Cs1—O3 ⁱⁱ	155.60 (4)	O5—As2—O7	114.48 (10)
O7—Cs1—O3 ⁱⁱ	96.43 (4)	O6—As2—O7	104.36 (9)
O6 ⁱ —Cs1—O10 ⁱ	36.71 (4)	O5—As2—O8	109.24 (9)
O2 ⁱⁱ —Cs1—O10 ⁱ	36.59 (4)	O6—As2—O8	109.46 (9)
O3 ⁱⁱⁱ —Cs1—O10 ⁱ	120.83 (4)	O7—As2—O8	107.84 (11)

O4—Cs1—O10 ⁱ	154.48 (4)	O5—As2—Cs1 ^x	95.67 (6)
O5 ^{iv} —Cs1—O10 ⁱ	136.79 (4)	O6—As2—Cs1 ^x	22.81 (6)
O1 ^v —Cs1—O10 ⁱ	50.52 (4)	O7—As2—Cs1 ^x	126.99 (7)
O11 ^{vi} —Cs1—O10 ⁱ	94.57 (4)	O8—As2—Cs1 ^x	101.01 (7)
O12—Cs1—O10 ⁱ	92.99 (4)	O5—As2—Cs1 ⁱⁱⁱ	26.12 (6)
O9 ^{vii} —Cs1—O10 ⁱ	102.35 (3)	O6—As2—Cs1 ⁱⁱⁱ	114.54 (6)
O11 ^{viii} —Cs1—O10 ⁱ	93.21 (4)	O7—As2—Cs1 ⁱⁱⁱ	132.54 (7)
O8—Cs1—O10 ⁱ	154.64 (4)	O8—As2—Cs1 ⁱⁱⁱ	84.33 (7)
O7 ^{vii} —Cs1—O10 ⁱ	68.01 (4)	Cs1 ^x —As2—Cs1 ⁱⁱⁱ	93.09 (2)
O12 ^{vi} —Cs1—O10 ⁱ	90.61 (3)	O5—As2—Cs1	134.76 (6)
O7—Cs1—O10 ⁱ	114.28 (4)	O6—As2—Cs1	113.69 (6)
O3 ⁱⁱ —Cs1—O10 ⁱ	73.06 (3)	O7—As2—Cs1	58.21 (8)
O6 ⁱ —Cs1—As1 ⁱⁱ	86.45 (4)	O8—As2—Cs1	50.09 (7)
O2 ⁱⁱ —Cs1—As1 ⁱⁱ	19.64 (3)	Cs1 ^x —As2—Cs1	125.199 (14)
O3 ⁱⁱⁱ —Cs1—As1 ⁱⁱ	71.16 (4)	Cs1 ⁱⁱⁱ —As2—Cs1	121.926 (14)
O4—Cs1—As1 ⁱⁱ	121.53 (3)	O5—As2—Cs1 ^{vii}	90.42 (6)
O5 ^{iv} —Cs1—As1 ⁱⁱ	164.43 (3)	O6—As2—Cs1 ^{vii}	86.22 (6)
O1 ^v —Cs1—As1 ⁱⁱ	50.57 (3)	O7—As2—Cs1 ^{vii}	39.15 (8)
O11 ^{vi} —Cs1—As1 ⁱⁱ	116.08 (4)	O8—As2—Cs1 ^{vii}	146.97 (7)
O12—Cs1—As1 ⁱⁱ	130.88 (4)	Cs1 ^x —As2—Cs1 ^{vii}	103.191 (16)
O9 ^{vii} —Cs1—As1 ⁱⁱ	69.65 (3)	Cs1 ⁱⁱⁱ —As2—Cs1 ^{vii}	116.209 (15)
O11 ^{viii} —Cs1—As1 ⁱⁱ	71.36 (3)	Cs1—As2—Cs1 ^{vii}	97.20 (2)
O8—Cs1—As1 ⁱⁱ	123.41 (3)	O9—As3—O10	116.43 (9)
O7 ^{vii} —Cs1—As1 ⁱⁱ	77.50 (3)	O9—As3—O12	107.64 (10)
O12 ^{vi} —Cs1—As1 ⁱⁱ	137.57 (3)	O10—As3—O12	110.13 (9)
O7—Cs1—As1 ⁱⁱ	104.25 (3)	O9—As3—O11	112.01 (9)
O3 ⁱⁱ —Cs1—As1 ⁱⁱ	23.02 (2)	O10—As3—O11	104.28 (9)
O10 ⁱ —Cs1—As1 ⁱⁱ	50.06 (2)	O12—As3—O11	105.88 (12)
O6 ⁱ —Cs1—As3 ^{vi}	64.95 (4)	O9—As3—Cs1 ^{vi}	140.88 (6)
O2 ⁱⁱ —Cs1—As3 ^{vi}	122.08 (3)	O10—As3—Cs1 ^{vi}	101.00 (6)
O3 ⁱⁱⁱ —Cs1—As3 ^{vi}	138.36 (4)	O12—As3—Cs1 ^{vi}	66.54 (9)
O4—Cs1—As3 ^{vi}	79.54 (3)	O11—As3—Cs1 ^{vi}	43.34 (8)
O5 ^{iv} —Cs1—As3 ^{vi}	71.42 (3)	O9—As3—Cs1 ^{xi}	85.37 (6)
O1 ^v —Cs1—As3 ^{vi}	75.01 (3)	O10—As3—Cs1 ^{xi}	88.31 (6)
O11 ^{vi} —Cs1—As3 ^{vi}	20.45 (4)	O12—As3—Cs1 ^{xi}	147.95 (8)
O12—Cs1—As3 ^{vi}	76.10 (5)	O11—As3—Cs1 ^{xi}	42.67 (9)
O9 ^{vii} —Cs1—As3 ^{vi}	166.23 (3)	Cs1 ^{vi} —As3—Cs1 ^{xi}	84.74 (3)
O11 ^{viii} —Cs1—As3 ^{vi}	77.68 (4)	O9—As3—Cs1	89.67 (6)
O8—Cs1—As3 ^{vi}	109.89 (3)	O10—As3—Cs1	104.40 (6)
O7 ^{vii} —Cs1—As3 ^{vi}	123.95 (4)	O12—As3—Cs1	25.37 (8)
O12 ^{vi} —Cs1—As3 ^{vi}	22.88 (3)	O11—As3—Cs1	130.41 (9)
O7—Cs1—As3 ^{vi}	128.41 (3)	Cs1 ^{vi} —As3—Cs1	91.81 (3)
O3 ⁱⁱ —Cs1—As3 ^{vi}	135.12 (3)	Cs1 ^{xi} —As3—Cs1	167.258 (8)
O10 ⁱ —Cs1—As3 ^{vi}	87.72 (2)	O9—As3—Cs1 ^{vii}	34.48 (6)
As1 ⁱⁱ —Cs1—As3 ^{vi}	124.056 (16)	O10—As3—Cs1 ^{vii}	82.04 (6)
O6 ⁱ —Cs1—As1 ^v	60.99 (4)	O12—As3—Cs1 ^{vii}	121.00 (9)
O2 ⁱⁱ —Cs1—As1 ^v	66.46 (3)	O11—As3—Cs1 ^{vii}	127.34 (8)
O3 ⁱⁱⁱ —Cs1—As1 ^v	116.05 (4)	Cs1 ^{vi} —As3—Cs1 ^{vii}	170.584 (8)

O4—Cs1—As1 ^v	108.35 (4)	Cs1 ^{xi} —As3—Cs1 ^{vii}	86.46 (3)
O5 ^{iv} —Cs1—As1 ^v	131.91 (3)	Cs1—As3—Cs1 ^{vii}	96.08 (3)
O1 ^v —Cs1—As1 ^v	17.20 (3)	As1—O1—Cs1 ^v	125.63 (8)
O11 ^{vi} —Cs1—As1 ^v	55.56 (4)	As1—O1—Cs1	77.18 (6)
O12—Cs1—As1 ^v	117.41 (4)	Cs1 ^v —O1—Cs1	99.42 (4)
O9 ^{vii} —Cs1—As1 ^v	133.25 (3)	As1—O1—Cs1 ^{iv}	74.03 (6)
O11 ^{viii} —Cs1—As1 ^v	52.95 (3)	Cs1 ^v —O1—Cs1 ^{iv}	142.21 (4)
O8—Cs1—As1 ^v	158.75 (3)	Cs1—O1—Cs1 ^{iv}	117.40 (4)
O7 ^{vii} —Cs1—As1 ^v	114.39 (3)	As1—O2—Cs1 ^{ix}	120.56 (9)
O12 ^{vi} —Cs1—As1 ^v	77.99 (3)	As1—O2—Cs1 ^v	78.93 (6)
O7—Cs1—As1 ^v	160.62 (3)	Cs1 ^{ix} —O2—Cs1 ^v	157.86 (5)
O3 ⁱⁱ —Cs1—As1 ^v	77.62 (3)	As1—O2—H2	111 (3)
O10 ⁱ —Cs1—As1 ^v	46.39 (3)	Cs1 ^{ix} —O2—H2	99 (3)
As1 ⁱⁱ —Cs1—As1 ^v	63.620 (14)	Cs1 ^v —O2—H2	81 (3)
As3 ^{vi} —Cs1—As1 ^v	60.497 (15)	As1—O3—Cs1 ^{iv}	140.95 (9)
O6 ⁱ —Cs1—O2 ^v	41.82 (4)	As1—O3—Cs1 ^{ix}	86.03 (7)
O2 ⁱⁱ —Cs1—O2 ^v	72.98 (2)	Cs1 ^{iv} —O3—Cs1 ^{ix}	131.45 (5)
O3 ⁱⁱⁱ —Cs1—O2 ^v	137.48 (4)	As1—O3—H3	110 (3)
O4—Cs1—O2 ^v	117.24 (4)	Cs1 ^{iv} —O3—H3	84 (3)
O5 ^{iv} —Cs1—O2 ^v	117.36 (4)	Cs1 ^{ix} —O3—H3	90 (3)
O1 ^v —Cs1—O2 ^v	38.27 (4)	As1—O4—Cs1	136.90 (8)
O11 ^{vi} —Cs1—O2 ^v	53.08 (4)	As1—O4—Cs1 ^{ix}	61.45 (5)
O12—Cs1—O2 ^v	95.87 (4)	Cs1—O4—Cs1 ^{ix}	145.93 (5)
O9 ^{vii} —Cs1—O2 ^v	142.89 (3)	As1—O4—H4	107 (2)
O11 ^{viii} —Cs1—O2 ^v	72.01 (4)	Cs1—O4—H4	109 (2)
O8—Cs1—O2 ^v	159.03 (4)	Cs1 ^{ix} —O4—H4	45 (2)
O7 ^{vii} —Cs1—O2 ^v	103.84 (4)	As2—O5—Cs1 ⁱⁱⁱ	141.07 (8)
O12 ^{vi} —Cs1—O2 ^v	61.15 (4)	As2—O5—Cs1 ^x	65.44 (6)
O7—Cs1—O2 ^v	146.83 (4)	Cs1 ⁱⁱⁱ —O5—Cs1 ^x	106.13 (4)
O3 ⁱⁱ —Cs1—O2 ^v	95.30 (4)	As2—O6—Cs1 ^x	145.08 (8)
O10 ⁱ —Cs1—O2 ^v	41.49 (3)	As2—O6—H6	112 (3)
As1 ⁱⁱ —Cs1—O2 ^v	77.02 (3)	Cs1 ^x —O6—H6	102 (3)
As3 ^{vi} —Cs1—O2 ^v	49.19 (2)	As2—O7—Cs1 ^{vii}	125.00 (10)
As1 ^v —Cs1—O2 ^v	21.54 (2)	As2—O7—Cs1	101.06 (9)
O6 ⁱ —Cs1—H8	127.7 (6)	Cs1 ^{vii} —O7—Cs1	133.62 (5)
O2 ⁱⁱ —Cs1—H8	137.8 (6)	As2—O7—H7	108 (3)
O3 ⁱⁱⁱ —Cs1—H8	67.3 (6)	Cs1 ^{vii} —O7—H7	103 (3)
O4—Cs1—H8	48.7 (6)	Cs1—O7—H7	63 (3)
O5 ^{iv} —Cs1—H8	31.8 (6)	As2—O8—Cs1	110.08 (9)
O1 ^v —Cs1—H8	153.0 (6)	As2—O8—Cs1 ⁱⁱⁱ	74.96 (6)
O11 ^{vi} —Cs1—H8	99.6 (6)	Cs1—O8—Cs1 ⁱⁱⁱ	142.44 (5)
O12—Cs1—H8	67.3 (6)	As2—O8—H8	110 (3)
O9 ^{vii} —Cs1—H8	67.9 (6)	Cs1—O8—H8	57 (3)
O11 ^{viii} —Cs1—H8	110.2 (6)	Cs1 ⁱⁱⁱ —O8—H8	159 (3)
O8—Cs1—H8	11.4 (6)	As3—O9—Cs1 ^{vii}	130.90 (8)
O7 ^{vii} —Cs1—H8	89.8 (6)	As3—O9—Cs1 ^{xi}	75.31 (6)
O12 ^{vi} —Cs1—H8	87.5 (6)	Cs1 ^{vii} —O9—Cs1 ^{xi}	99.91 (4)
O7—Cs1—H8	44.8 (6)	As3—O10—Cs1 ^x	168.61 (9)

O3 ⁱⁱ —Cs1—H8	114.7 (6)	As3—O10—Cs1 ^{vi}	59.93 (5)
O10 ⁱ —Cs1—H8	156.5 (6)	Cs1 ^x —O10—Cs1 ^{vi}	111.15 (3)
As1 ⁱⁱ —Cs1—H8	134.8 (6)	As3—O10—Cs1 ^{vii}	78.77 (6)
As3 ^{vi} —Cs1—H8	99.2 (6)	Cs1 ^x —O10—Cs1 ^{vii}	110.89 (3)
As1 ^v —Cs1—H8	154.2 (6)	Cs1 ^{vi} —O10—Cs1 ^{vii}	137.79 (4)
O2 ^v —Cs1—H8	148.0 (6)	As3—O10—Cs1 ^{xi}	72.57 (6)
O6 ⁱ —Cs1—H12	72.2 (7)	Cs1 ^x —O10—Cs1 ^{xi}	113.62 (3)
O2 ⁱⁱ —Cs1—H12	123.9 (7)	Cs1 ^{vi} —O10—Cs1 ^{xi}	76.59 (3)
O3 ⁱⁱⁱ —Cs1—H12	118.9 (6)	Cs1 ^{vii} —O10—Cs1 ^{xi}	83.52 (4)
O4—Cs1—H12	91.9 (7)	As3—O11—Cs1 ^{vi}	116.21 (11)
O5 ^{iv} —Cs1—H12	32.8 (7)	As3—O11—Cs1 ^{xi}	119.34 (11)
O1 ^v —Cs1—H12	141.8 (6)	Cs1 ^{vi} —O11—Cs1 ^{xi}	121.90 (6)
O11 ^{vi} —Cs1—H12	91.0 (6)	As3—O11—H11	115 (3)
O12—Cs1—H12	13.3 (7)	Cs1 ^{vi} —O11—H11	102 (3)
O9 ^{vii} —Cs1—H12	93.7 (6)	Cs1 ^{xi} —O11—H11	68 (3)
O11 ^{viii} —Cs1—H12	145.1 (6)	As3—O12—Cs1	142.50 (11)
O8—Cs1—H12	63.9 (6)	As3—O12—Cs1 ^{vi}	90.58 (9)
O7 ^{vii} —Cs1—H12	66.1 (6)	Cs1—O12—Cs1 ^{vi}	126.73 (6)
O12 ^{vi} —Cs1—H12	51.9 (6)	As3—O12—H12	110 (3)
O7—Cs1—H12	55.3 (6)	Cs1—O12—H12	68 (3)
O3 ⁱⁱ —Cs1—H12	149.4 (6)	Cs1 ^{vi} —O12—H12	95 (3)
O10 ⁱ —Cs1—H12	105.9 (7)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O10 ^{viii}	0.83 (4)	1.70 (4)	2.524 (2)	171 (4)
O3—H3 \cdots O9 ^x	0.79 (4)	1.76 (4)	2.553 (3)	172 (4)
O4—H4 \cdots O1 ⁱⁱⁱ	0.92 (3)	1.70 (3)	2.609 (2)	170 (3)
O6—H6 \cdots O10	0.91 (2)	1.64 (2)	2.539 (2)	170 (4)
O7—H7 \cdots O9 ^{vii}	0.81 (4)	1.79 (4)	2.599 (3)	177 (4)
O11—H11 \cdots O1 ^{vi}	0.79 (4)	1.85 (4)	2.630 (3)	168 (4)
O8—H8 \cdots O5 ^{iv}	0.82 (4)	1.85 (4)	2.664 (2)	170 (4)
O12—H12 \cdots O5 ^{iv}	0.81 (4)	1.84 (4)	2.643 (3)	171 (4)

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

Dilithium bis(dihydrogen phosphate) (Li₂H₂PO₄)₂

Crystal data

Li₂(H₂PO₄)₂

$M_r = 207.85$

Monoclinic, $P2_1/n$

$a = 5.400$ (1) \AA

$b = 15.927$ (3) \AA

$c = 7.562$ (2) \AA

$\beta = 90.47$ (3) $^\circ$

$V = 650.4$ (2) \AA^3

$Z = 4$

$F(000) = 416$

$D_x = 2.123$ Mg m^{-3}

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

Cell parameters from 2948 reflections

$\theta = 2.6\text{--}34.9^\circ$

$\mu = 0.67 \text{ mm}^{-1}$
 $T = 293 \text{ K}$

Crude blocky, colourless
 $0.15 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan (SCALEPACK; Otwinowski *et al.*, 2003)

$T_{\min} = 0.906$, $T_{\max} = 0.936$

5625 measured reflections

2857 independent reflections

2490 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\max} = 34.9^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -8 \rightarrow 8$

$k = -25 \rightarrow 25$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.072$

$S = 1.04$

2857 reflections

126 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.2847P]$

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

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

$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL2016

(Sheldrick, 2015),

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

Extinction coefficient: 0.032 (2)

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	0.3095 (4)	0.41644 (13)	0.8697 (3)	0.0180 (3)
Li2	0.2049 (4)	0.17789 (12)	0.3787 (3)	0.0188 (4)
P1	0.20738 (5)	0.22094 (2)	0.78828 (3)	0.01221 (6)
P2	0.82490 (4)	0.50113 (2)	0.75280 (3)	0.01103 (6)
O1	0.31754 (15)	0.18533 (5)	0.62305 (11)	0.02001 (15)
O2	0.35275 (14)	0.28897 (5)	0.88008 (11)	0.01756 (14)
O3	0.16657 (18)	0.15302 (6)	0.93356 (12)	0.02388 (18)
O4	-0.06014 (14)	0.25573 (6)	0.73730 (11)	0.01953 (15)
O5	0.64679 (14)	0.43820 (5)	0.82463 (11)	0.01765 (14)
O6	1.07946 (14)	0.46742 (5)	0.71115 (10)	0.01685 (14)
O7	0.71704 (16)	0.54689 (6)	0.58619 (11)	0.02046 (16)
O8	0.84346 (15)	0.57281 (5)	0.89622 (10)	0.01729 (14)
H1	0.057 (4)	0.1225 (14)	0.916 (3)	0.055 (7)*
H2	-0.089 (4)	0.2448 (15)	0.630 (3)	0.056 (6)*
H3	0.782 (5)	0.5391 (16)	0.503 (3)	0.064 (8)*
H4	0.950 (4)	0.6050 (14)	0.874 (3)	0.052 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li1	0.0137 (8)	0.0215 (9)	0.0189 (8)	0.0019 (7)	0.0014 (6)	0.0024 (7)
Li2	0.0161 (8)	0.0181 (8)	0.0222 (9)	-0.0015 (6)	0.0007 (7)	-0.0005 (7)
P1	0.01114 (11)	0.01204 (11)	0.01341 (11)	0.00015 (7)	-0.00151 (8)	-0.00139 (8)
P2	0.01011 (11)	0.01230 (11)	0.01071 (11)	0.00059 (7)	0.00120 (7)	0.00032 (7)
O1	0.0202 (4)	0.0236 (4)	0.0162 (3)	0.0080 (3)	-0.0008 (3)	-0.0041 (3)
O2	0.0152 (3)	0.0149 (3)	0.0225 (4)	-0.0028 (2)	-0.0017 (3)	-0.0042 (3)
O3	0.0271 (4)	0.0227 (4)	0.0217 (4)	-0.0094 (3)	-0.0068 (3)	0.0077 (3)
O4	0.0137 (3)	0.0284 (4)	0.0164 (3)	0.0063 (3)	-0.0032 (2)	-0.0035 (3)
O5	0.0141 (3)	0.0152 (3)	0.0237 (4)	-0.0032 (2)	0.0036 (3)	0.0019 (3)
O6	0.0124 (3)	0.0245 (4)	0.0137 (3)	0.0057 (3)	0.0018 (2)	0.0025 (3)
O7	0.0208 (4)	0.0280 (4)	0.0126 (3)	0.0118 (3)	0.0016 (3)	0.0033 (3)
O8	0.0207 (4)	0.0166 (3)	0.0147 (3)	-0.0055 (3)	0.0046 (3)	-0.0041 (2)

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

Li1—O5	1.888 (2)	P1—O2	1.5043 (8)
Li1—O6 ⁱ	1.902 (2)	P1—O3	1.5588 (9)
Li1—O8 ⁱⁱ	1.967 (2)	P1—O4	1.5917 (8)
Li1—O2	2.045 (2)	P2—O5	1.4944 (8)
Li1—Li2 ⁱⁱⁱ	2.611 (3)	P2—O6	1.5113 (8)
Li1—P2 ⁱ	3.068 (2)	P2—O7	1.5640 (9)
Li2—O5 ^{iv}	1.919 (2)	P2—O8	1.5774 (8)
Li2—O1	1.944 (2)	O3—H1	0.77 (2)
Li2—O4 ^v	1.973 (2)	O4—H2	0.84 (2)
Li2—O2 ^{iv}	1.974 (2)	O7—H3	0.73 (2)
Li2—P2 ^{iv}	3.077 (2)	O8—H4	0.79 (2)
P1—O1	1.4996 (9)		
O5—Li1—O6 ⁱ	115.73 (11)	O2—P1—O4	109.28 (5)
O5—Li1—O8 ⁱⁱ	124.03 (11)	O3—P1—O4	106.20 (5)
O6 ⁱ —Li1—O8 ⁱⁱ	104.66 (10)	O5—P2—O6	115.26 (5)
O5—Li1—O2	94.55 (9)	O5—P2—O7	111.65 (5)
O6 ⁱ —Li1—O2	121.45 (11)	O6—P2—O7	109.33 (5)
O8 ⁱⁱ —Li1—O2	95.77 (9)	O5—P2—O8	105.84 (5)
O5—Li1—Li2 ⁱⁱⁱ	47.19 (7)	O6—P2—O8	110.34 (5)
O6 ⁱ —Li1—Li2 ⁱⁱⁱ	142.36 (11)	O7—P2—O8	103.75 (5)
O8 ⁱⁱ —Li1—Li2 ⁱⁱⁱ	112.09 (10)	O5—P2—Li1 ^{vi}	98.65 (5)
O2—Li1—Li2 ⁱⁱⁱ	48.30 (6)	O6—P2—Li1 ^{vi}	29.39 (5)
O5—Li1—P2 ⁱ	133.57 (9)	O7—P2—Li1 ^{vi}	138.44 (5)
O6 ⁱ —Li1—P2 ⁱ	22.95 (4)	O8—P2—Li1 ^{vi}	94.06 (5)
O8 ⁱⁱ —Li1—P2 ⁱ	81.81 (7)	O5—P2—Li2 ⁱⁱⁱ	29.33 (5)
O2—Li1—P2 ⁱ	122.98 (9)	O6—P2—Li2 ⁱⁱⁱ	85.96 (5)
Li2 ⁱⁱⁱ —Li1—P2 ⁱ	162.91 (9)	O7—P2—Li2 ⁱⁱⁱ	127.10 (6)
O5 ^{iv} —Li2—O1	108.09 (10)	O8—P2—Li2 ⁱⁱⁱ	118.06 (5)
O5 ^{iv} —Li2—O4 ^v	120.38 (11)	Li1 ^{vi} —P2—Li2 ⁱⁱⁱ	71.62 (5)

O1—Li2—O4 ^v	106.56 (10)	P1—O1—Li2	133.78 (8)
O5 ^{iv} —Li2—O2 ^{iv}	95.90 (9)	P1—O2—Li2 ⁱⁱⁱ	133.57 (8)
O1—Li2—O2 ^{iv}	105.81 (10)	P1—O2—Li1	129.67 (8)
O4 ^v —Li2—O2 ^{iv}	118.91 (11)	Li2 ⁱⁱⁱ —O2—Li1	81.02 (8)
O5 ^{iv} —Li2—Li1 ^{iv}	46.19 (7)	P1—O3—H1	115.4 (17)
O1—Li2—Li1 ^{iv}	108.00 (10)	P1—O4—Li2 ^{vii}	129.92 (8)
O4 ^v —Li2—Li1 ^{iv}	145.44 (11)	P1—O4—H2	108.9 (16)
O2 ^{iv} —Li2—Li1 ^{iv}	50.68 (7)	Li2 ^{vii} —O4—H2	121.0 (16)
O5 ^{iv} —Li2—P2 ^{iv}	22.43 (4)	P2—O5—Li1	144.45 (8)
O1—Li2—P2 ^{iv}	106.59 (8)	P2—O5—Li2 ⁱⁱⁱ	128.24 (8)
O4 ^v —Li2—P2 ^{iv}	101.01 (8)	Li1—O5—Li2 ⁱⁱⁱ	86.62 (9)
O2 ^{iv} —Li2—P2 ^{iv}	117.05 (8)	P2—O6—Li1 ^{vi}	127.66 (8)
Li1 ^{iv} —Li2—P2 ^{iv}	68.47 (6)	P2—O7—H3	116 (2)
O1—P1—O2	116.61 (5)	P2—O8—Li1 ⁱⁱ	131.07 (8)
O1—P1—O3	112.58 (5)	P2—O8—H4	111.6 (17)
O2—P1—O3	104.53 (5)	Li1 ⁱⁱ —O8—H4	116.4 (17)
O1—P1—O4	107.18 (5)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1 \cdots O7 ^{viii}	0.77 (2)	1.91 (2)	2.6769 (12)	171 (2)
O4—H2 \cdots O2 ^{iv}	0.84 (2)	1.99 (2)	2.8292 (14)	176 (2)
O7—H3 \cdots O6 ^{ix}	0.73 (2)	1.79 (2)	2.5210 (13)	172 (3)
O8—H4 \cdots O1 ^x	0.79 (2)	1.79 (2)	2.5667 (12)	167 (2)

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

Ammonium dihydrogen arsenate(V) trihydrogen arsenate(V) (NH₄H₂AsO₄H₃AsO₄)

Crystal data

(NH₄)(H₂AsO₄)(H₃AsO₄)

$M_r = 300.92$

Orthorhombic, *Pbca*

$a = 7.943$ (2) \AA

$b = 9.855$ (2) \AA

$c = 19.623$ (4) \AA

$V = 1536.1$ (6) \AA^3

$Z = 8$

$F(000) = 1168$

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan

(SCALEPACK; Otwinowski *et al.*, 2003)

$T_{\min} = 0.355, T_{\max} = 0.581$

1799 measured reflections

$D_x = 2.602$ Mg m⁻³

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

Cell parameters from 793 reflections

$\theta = 3.3\text{--}28.7^\circ$

$\mu = 8.71$ mm⁻¹

$T = 293$ K

Rounded prisms, colourless

$0.15 \times 0.10 \times 0.07$ mm

1295 independent reflections

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

$R_{\text{int}} = 0.038$

$\theta_{\max} = 28.7^\circ, \theta_{\min} = 3.3^\circ$

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 12$

$l = -25 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.109$

$S = 1.02$

1295 reflections

136 parameters

9 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 1.4516P]$

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

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

$\Delta\rho_{\max} = 0.74 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL2016

(Sheldrick, 2015),

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

Extinction coefficient: 0.0011 (5)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
N	0.2990 (9)	0.5958 (9)	-0.1213 (4)	0.0333 (17)
As1	0.19665 (8)	0.31360 (8)	0.03568 (4)	0.0228 (2)
As2	0.26446 (8)	0.39549 (9)	-0.27893 (4)	0.0254 (3)
O1	0.2714 (6)	0.1598 (5)	0.0226 (3)	0.0266 (13)
O2	0.0736 (6)	0.3271 (5)	0.1038 (3)	0.0296 (13)
O3	0.0971 (6)	0.3697 (6)	-0.0359 (3)	0.0302 (13)
O4	0.3684 (6)	0.4183 (6)	0.0407 (3)	0.0305 (14)
O5	0.2149 (6)	0.3602 (6)	-0.2002 (3)	0.0287 (13)
O6	0.3472 (7)	0.5542 (6)	-0.2792 (3)	0.0351 (14)
O7	0.0911 (6)	0.3961 (6)	-0.3291 (3)	0.0344 (14)
O8	0.4036 (6)	0.2901 (6)	-0.3172 (3)	0.0364 (16)
H1	0.410 (3)	0.585 (11)	-0.121 (6)	0.08 (4)*
H2	0.264 (10)	0.522 (6)	-0.145 (4)	0.040*
H3	0.251 (11)	0.619 (11)	-0.082 (3)	0.06 (3)*
H4	0.260 (19)	0.667 (11)	-0.146 (7)	0.18 (9)*
H5	0.013 (13)	0.430 (12)	-0.039 (8)	0.16 (7)*
H7	0.37 (2)	0.57 (2)	-0.324 (2)	0.22 (9)*
H6	0.332 (8)	0.502 (4)	0.032 (4)	0.03 (2)*
H8	0.057 (10)	0.324 (6)	-0.352 (4)	0.05 (3)*
H9	0.494 (9)	0.333 (12)	-0.300 (6)	0.10 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N	0.035 (4)	0.039 (5)	0.026 (4)	-0.001 (3)	0.002 (3)	-0.009 (4)
As1	0.0201 (4)	0.0169 (4)	0.0313 (5)	0.0005 (3)	0.0001 (3)	-0.0001 (4)
As2	0.0228 (4)	0.0240 (5)	0.0292 (5)	-0.0018 (3)	0.0014 (3)	-0.0014 (4)

O1	0.025 (3)	0.017 (3)	0.038 (4)	-0.0009 (19)	0.006 (2)	-0.006 (3)
O2	0.027 (2)	0.025 (3)	0.036 (4)	0.005 (2)	0.003 (2)	-0.004 (3)
O3	0.025 (3)	0.032 (3)	0.033 (3)	0.003 (2)	-0.003 (2)	0.006 (3)
O4	0.022 (2)	0.018 (3)	0.051 (4)	-0.001 (2)	-0.003 (2)	0.002 (3)
O5	0.026 (3)	0.030 (3)	0.030 (3)	-0.003 (2)	0.004 (2)	0.002 (3)
O6	0.041 (3)	0.025 (3)	0.039 (4)	0.000 (2)	-0.003 (2)	-0.002 (3)
O7	0.024 (3)	0.039 (4)	0.040 (4)	0.000 (2)	-0.010 (2)	-0.003 (3)
O8	0.022 (3)	0.031 (3)	0.056 (5)	0.001 (2)	0.007 (2)	-0.012 (3)

Geometric parameters (Å, °)

N—O5	2.869 (10)	N—H3	0.89 (2)
N—O1 ⁱ	2.947 (9)	N—H4	0.90 (2)
N—O5 ⁱ	3.032 (11)	As1—O1	1.648 (5)
N—O2 ⁱⁱ	3.075 (9)	As1—O2	1.662 (6)
N—O4 ⁱⁱⁱ	3.082 (9)	As1—O3	1.705 (6)
N—O6	3.148 (10)	As1—O4	1.714 (5)
N—O7 ^{iv}	3.194 (10)	As2—O5	1.632 (6)
N—O3	3.216 (10)	As2—O8	1.692 (5)
N—O8 ^v	3.272 (9)	As2—O7	1.693 (5)
N—O3 ⁱ	3.283 (10)	As2—O6	1.696 (6)
N—O4	3.671 (11)	As2—H9	1.97 (10)
N—As2	3.679 (8)	O3—H5	0.89 (2)
N—As1 ⁱ	3.755 (8)	O4—H6	0.89 (2)
N—O6 ^{vi}	4.106 (10)	O6—H7	0.90 (2)
N—As1	4.229 (9)	O7—H8	0.89 (2)
N—H1	0.89 (2)	O8—H9	0.89 (2)
N—H2	0.91 (2)		
O5—N—O1 ⁱ	130.2 (3)	O2—As1—O3	111.4 (3)
O5—N—O5 ⁱ	114.3 (3)	O1—As1—O4	106.0 (2)
O1 ⁱ —N—O5 ⁱ	107.3 (3)	O2—As1—O4	111.9 (3)
O5—N—O2 ⁱⁱ	92.1 (2)	O3—As1—O4	102.8 (3)
O1 ⁱ —N—O2 ⁱⁱ	70.0 (2)	O1—As1—N ^{vii}	48.9 (2)
O5 ⁱ —N—O2 ⁱⁱ	79.0 (2)	O2—As1—N ^{vii}	135.4 (2)
O5—N—O4 ⁱⁱⁱ	116.1 (3)	O3—As1—N ^{vii}	60.9 (2)
O1 ⁱ —N—O4 ⁱⁱⁱ	71.4 (2)	O4—As1—N ^{vii}	112.6 (2)
O5 ⁱ —N—O4 ⁱⁱⁱ	109.4 (3)	O1—As1—N	114.9 (2)
O2 ⁱⁱ —N—O4 ⁱⁱⁱ	141.2 (3)	O2—As1—N	130.3 (2)
O5—N—O6	52.6 (2)	O3—As1—N	43.6 (2)
O1 ⁱ —N—O6	173.6 (4)	O4—As1—N	59.5 (2)
O5 ⁱ —N—O6	67.3 (2)	N ^{vii} —As1—N	77.08 (15)
O2 ⁱⁱ —N—O6	105.0 (3)	O1—As1—N ⁱⁱ	124.9 (2)
O4 ⁱⁱⁱ —N—O6	113.3 (3)	O2—As1—N ⁱⁱ	31.2 (2)
O5—N—O7 ^{iv}	60.4 (2)	O3—As1—N ⁱⁱ	80.4 (2)
O1 ⁱ —N—O7 ^{iv}	124.2 (3)	O4—As1—N ⁱⁱ	124.9 (2)
O5 ⁱ —N—O7 ^{iv}	113.6 (3)	N ^{vii} —As1—N ⁱⁱ	116.13 (17)
O2 ⁱⁱ —N—O7 ^{iv}	152.3 (3)	N—As1—N ⁱⁱ	108.59 (12)

O4 ⁱⁱⁱ —N—O7 ^{iv}	60.4 (2)	O1—As1—N ⁱⁱⁱ	85.3 (2)
O6—N—O7 ^{iv}	62.1 (2)	O2—As1—N ⁱⁱⁱ	102.1 (2)
O5—N—O3	66.7 (2)	O3—As1—N ⁱⁱⁱ	131.8 (2)
O1 ⁱ —N—O3	63.5 (2)	O4—As1—N ⁱⁱⁱ	30.4 (2)
O5 ⁱ —N—O3	147.5 (3)	N ^{vii} —As1—N ⁱⁱⁱ	114.68 (18)
O2 ⁱⁱ —N—O3	68.5 (2)	N—As1—N ⁱⁱⁱ	88.28 (16)
O4 ⁱⁱⁱ —N—O3	97.4 (3)	N ⁱⁱ —As1—N ⁱⁱⁱ	128.79 (19)
O6—N—O3	118.9 (3)	O1—As1—N ^{viii}	64.6 (2)
O7 ^{iv} —N—O3	95.4 (3)	O2—As1—N ^{viii}	57.6 (2)
O5—N—O8 ^v	116.3 (3)	O3—As1—N ^{viii}	103.2 (2)
O1 ⁱ —N—O8 ^v	111.4 (3)	O4—As1—N ^{viii}	154.0 (2)
O5 ⁱ —N—O8 ^v	48.33 (18)	N ^{vii} —As1—N ^{viii}	80.41 (16)
O2 ⁱⁱ —N—O8 ^v	126.3 (3)	N—As1—N ^{viii}	146.26 (12)
O4 ⁱⁱⁱ —N—O8 ^v	66.2 (2)	N ⁱⁱ —As1—N ^{viii}	60.37 (8)
O6—N—O8 ^v	68.0 (2)	N ⁱⁱⁱ —As1—N ^{viii}	124.17 (18)
O7 ^{iv} —N—O8 ^v	74.0 (2)	O5—As2—O8	116.5 (3)
O3—N—O8 ^v	163.3 (3)	O5—As2—O7	110.8 (3)
O5—N—O3 ⁱ	177.9 (3)	O8—As2—O7	106.0 (3)
O1 ⁱ —N—O3 ⁱ	51.9 (2)	O5—As2—O6	107.0 (3)
O5 ⁱ —N—O3 ⁱ	64.1 (2)	O8—As2—O6	108.2 (3)
O2 ⁱⁱ —N—O3 ⁱ	89.0 (2)	O7—As2—O6	108.1 (3)
O4 ⁱⁱⁱ —N—O3 ⁱ	63.9 (2)	O5—As2—N	48.4 (2)
O6—N—O3 ⁱ	125.4 (3)	O8—As2—N	130.8 (2)
O7 ^{iv} —N—O3 ⁱ	118.7 (3)	O7—As2—N	123.2 (2)
O3—N—O3 ⁱ	115.4 (3)	O6—As2—N	58.6 (3)
O8 ^v —N—O3 ⁱ	61.7 (2)	O5—As2—N ^{vii}	31.3 (2)
O5—N—O4	96.7 (3)	O8—As2—N ^{vii}	88.5 (2)
O1 ⁱ —N—O4	45.61 (18)	O7—As2—N ^{vii}	108.9 (2)
O5 ⁱ —N—O4	149.0 (3)	O6—As2—N ^{vii}	132.8 (3)
O2 ⁱⁱ —N—O4	99.5 (2)	N—As2—N ^{vii}	76.88 (15)
O4 ⁱⁱⁱ —N—O4	53.5 (2)	O5—As2—N ^{vi}	107.4 (2)
O6—N—O4	140.5 (3)	O8—As2—N ^{vi}	126.6 (2)
O7 ^{iv} —N—O4	82.0 (2)	O7—As2—N ^{vi}	26.1 (2)
O3—N—O4	45.05 (17)	O6—As2—N ^{vi}	85.1 (2)
O8 ^v —N—O4	119.3 (2)	N—As2—N ^{vi}	100.7 (2)
O3 ⁱ —N—O4	84.9 (2)	N ^{vii} —As2—N ^{vi}	120.20 (9)
O5—N—As2	25.19 (13)	O5—As2—N ^{ix}	114.5 (2)
O1 ⁱ —N—As2	155.0 (3)	O8—As2—N ^{ix}	4.0 (2)
O5 ⁱ —N—As2	91.7 (2)	O7—As2—N ^{ix}	110.0 (2)
O2 ⁱⁱ —N—As2	98.9 (2)	O6—As2—N ^{ix}	106.1 (2)
O4 ⁱⁱⁱ —N—As2	118.1 (3)	N—As2—N ^{ix}	126.83 (8)
O6—N—As2	27.38 (13)	N ^{vii} —As2—N ^{ix}	87.52 (18)
O7 ^{iv} —N—As2	57.81 (17)	N ^{vi} —As2—N ^{ix}	130.26 (19)
O3—N—As2	91.7 (2)	O5—As2—N ^{iv}	130.53 (19)
O8 ^v —N—As2	93.3 (2)	O8—As2—N ^{iv}	61.4 (2)
O3 ⁱ —N—As2	152.7 (3)	O7—As2—N ^{iv}	117.1 (2)
O4—N—As2	118.9 (3)	O6—As2—N ^{iv}	46.9 (2)
O5—N—As1 ⁱ	155.1 (3)	N—As2—N ^{iv}	93.05 (19)

O1 ⁱ —N—As1 ⁱ	24.94 (13)	N ^{vii} —As2—N ^{iv}	129.92 (9)
O5 ⁱ —N—As1 ⁱ	85.9 (2)	N ^{vi} —As2—N ^{iv}	109.85 (16)
O2 ⁱⁱ —N—As1 ⁱ	77.1 (2)	N ^{ix} —As2—N ^{iv}	59.62 (5)
O4 ⁱⁱⁱ —N—As1 ⁱ	66.22 (19)	O5—As2—N ^x	91.4 (2)
O6—N—As1 ⁱ	151.7 (3)	O8—As2—N ^x	92.4 (2)
O7 ^{iv} —N—As1 ⁱ	126.5 (3)	O7—As2—N ^x	33.3 (2)
O3—N—As1 ⁱ	88.5 (2)	O6—As2—N ^x	141.2 (2)
O8 ^v —N—As1 ⁱ	87.8 (2)	N—As2—N ^x	128.63 (8)
O3 ⁱ —N—As1 ⁱ	26.98 (12)	N ^{vii} —As2—N ^x	78.44 (17)
O4—N—As1 ⁱ	63.92 (16)	N ^{vi} —As2—N ^x	56.57 (5)
As2—N—As1 ⁱ	175.6 (2)	N ^{ix} —As2—N ^x	96.01 (15)
O5—N—O6 ^{vi}	57.27 (18)	N ^{iv} —As2—N ^x	136.46 (17)
O1 ⁱ —N—O6 ^{vi}	108.1 (2)	O5—As2—H9	111 (4)
O5 ⁱ —N—O6 ^{vi}	79.1 (2)	O8—As2—H9	26.9 (19)
O2 ⁱⁱ —N—O6 ^{vi}	40.23 (16)	O7—As2—H9	129 (3)
O4 ⁱⁱⁱ —N—O6 ^{vi}	171.4 (3)	O6—As2—H9	86 (3)
O6—N—O6 ^{vi}	68.00 (18)	N—As2—H9	106 (2)
O7 ^{iv} —N—O6 ^{vi}	115.4 (3)	N ^{vii} —As2—H9	93 (4)
O3—N—O6 ^{vi}	75.10 (19)	N ^{vi} —As2—H9	142 (4)
O8 ^v —N—O6 ^{vi}	120.9 (3)	N ^{ix} —As2—H9	23.3 (19)
O3 ⁱ —N—O6 ^{vi}	123.0 (3)	N ^{iv} —As2—H9	43 (4)
O4—N—O6 ^{vi}	119.7 (2)	N ^x —As2—H9	119.3 (19)
As2—N—O6 ^{vi}	58.77 (14)	As1—O1—N ^{vii}	106.1 (3)
As1 ⁱ —N—O6 ^{vi}	117.1 (2)	As1—O1—N ⁱⁱⁱ	73.8 (2)
O5—N—As1	79.4 (2)	N ^{vii} —O1—N ⁱⁱⁱ	131.0 (2)
O1 ⁱ —N—As1	53.58 (17)	As1—O1—N ^{viii}	97.7 (2)
O5 ⁱ —N—As1	158.4 (3)	N ^{vii} —O1—N ^{viii}	97.1 (2)
O2 ⁱⁱ —N—As1	84.0 (2)	N ⁱⁱⁱ —O1—N ^{viii}	131.9 (2)
O4 ⁱⁱⁱ —N—As1	76.2 (2)	As1—O1—N	48.2 (2)
O6—N—As1	130.9 (3)	N ^{vii} —O1—N	70.2 (2)
O7 ^{iv} —N—As1	87.5 (2)	N ⁱⁱⁱ —O1—N	76.27 (17)
O3—N—As1	21.42 (11)	N ^{viii} —O1—N	132.56 (18)
O8 ^v —N—As1	142.4 (3)	As1—O2—N ⁱⁱ	132.5 (3)
O3 ⁱ —N—As1	102.5 (2)	As1—O2—N ^{viii}	105.1 (2)
O4—N—As1	23.73 (9)	N ⁱⁱ —O2—N ^{viii}	76.41 (15)
As2—N—As1	104.2 (2)	As1—O2—N ⁱⁱⁱ	59.12 (17)
As1 ⁱ —N—As1	77.29 (15)	N ⁱⁱ —O2—N ⁱⁱⁱ	154.8 (3)
O6 ^{vi} —N—As1	96.48 (18)	N ^{viii} —O2—N ⁱⁱⁱ	125.74 (19)
O5—N—H1	98 (7)	As1—O2—N ^{vii}	31.33 (17)
O1 ⁱ —N—H1	102 (7)	N ⁱⁱ —O2—N ^{vii}	113.6 (2)
O5 ⁱ —N—H1	98 (7)	N ^{viii} —O2—N ^{vii}	76.03 (17)
O2 ⁱⁱ —N—H1	170 (7)	N ⁱⁱⁱ —O2—N ^{vii}	85.99 (16)
O4 ⁱⁱⁱ —N—H1	31 (7)	As1—O3—N	115.0 (3)
O6—N—H1	82 (7)	As1—O3—N ^{vii}	92.1 (3)
O7 ^{iv} —N—H1	37 (7)	N—O3—N ^{vii}	100.3 (2)
O3—N—H1	114 (8)	As1—O3—N ⁱⁱ	77.3 (2)
O8 ^v —N—H1	50 (7)	N—O3—N ⁱⁱ	131.7 (2)
O3 ⁱ —N—H1	81 (7)	N ^{vii} —O3—N ⁱⁱ	126.8 (2)

O4—N—H1	78 (8)	As1—O3—H5	128 (10)
As2—N—H1	91 (7)	N—O3—H5	83 (10)
As1 ⁱ —N—H1	93 (7)	N ^{vii} —O3—H5	135 (10)
O6 ^{vi} —N—H1	149 (7)	N ⁱⁱ —O3—H5	57 (10)
As1—N—H1	96 (8)	As1—O4—N ⁱⁱⁱ	133.2 (3)
O5—N—H2	4 (5)	As1—O4—N	96.7 (3)
O1 ⁱ —N—H2	128 (6)	N ⁱⁱⁱ —O4—N	126.5 (2)
O5 ⁱ —N—H2	114 (6)	As1—O4—N ^{vii}	47.7 (2)
O2 ⁱⁱ —N—H2	88 (5)	N ⁱⁱⁱ —O4—N ^{vii}	124.1 (2)
O4 ⁱⁱⁱ —N—H2	119 (6)	N—O4—N ^{vii}	72.12 (17)
O6—N—H2	55 (6)	As1—O4—H6	107 (5)
O7 ^{iv} —N—H2	65 (5)	N ⁱⁱⁱ —O4—H6	115 (5)
O3—N—H2	64 (6)	N—O4—H6	49 (6)
O8 ^v —N—H2	120 (5)	N ^{vii} —O4—H6	114 (6)
O3 ⁱ —N—H2	177 (5)	As2—O5—N	106.4 (3)
O4—N—H2	97 (6)	As2—O5—N ^{vii}	132.5 (3)
As2—N—H2	27 (6)	N—O5—N ^{vii}	115.4 (3)
As1 ⁱ —N—H2	152 (5)	As2—O6—N	94.0 (3)
O6 ^{vi} —N—H2	54 (5)	As2—O6—N ^{iv}	115.6 (3)
As1—N—H2	78 (6)	N—O6—N ^{iv}	124.1 (3)
H1—N—H2	102 (8)	As2—O6—N ^{vi}	74.2 (2)
O5—N—H3	125 (7)	N—O6—N ^{vi}	106.2 (3)
O1 ⁱ —N—H3	15 (6)	N ^{iv} —O6—N ^{vi}	126.3 (2)
O5 ⁱ —N—H3	102 (8)	As2—O6—H7	102 (10)
O2 ⁱⁱ —N—H3	55 (6)	N—O6—H7	164 (10)
O4 ⁱⁱⁱ —N—H3	86 (6)	N ^{iv} —O6—H7	50 (10)
O6—N—H3	160 (7)	N ^{vi} —O6—H7	76 (10)
O7 ^{iv} —N—H3	137 (7)	As2—O7—N ^{vi}	140.4 (3)
O3—N—H3	61 (7)	As2—O7—N ^x	134.4 (3)
O8 ^v —N—H3	119 (7)	N ^{vi} —O7—N ^x	80.52 (12)
O3 ⁱ —N—H3	57 (7)	As2—O7—N	39.73 (19)
O4—N—H3	56 (7)	N ^{vi} —O7—N	104.8 (3)
As2—N—H3	146 (7)	N ^x —O7—N	134.77 (17)
As1 ⁱ —N—H3	31 (7)	As2—O7—N ^{vii}	52.8 (2)
O6 ^{vi} —N—H3	94 (6)	N ^{vi} —O7—N ^{vii}	136.37 (19)
As1—N—H3	57 (8)	N ^x —O7—N ^{vii}	84.68 (19)
H1—N—H3	117 (9)	N—O7—N ^{vii}	60.22 (12)
H2—N—H3	122 (9)	As2—O7—H8	123 (6)
O5—N—H4	105 (10)	N ^{vi} —O7—H8	97 (6)
O1 ⁱ —N—H4	106 (10)	N ^x —O7—H8	29 (5)
O5 ⁱ —N—H4	18 (10)	N—O7—H8	150 (6)
O2 ⁱⁱ —N—H4	62 (10)	N ^{vii} —O7—H8	90 (6)
O4 ⁱⁱⁱ —N—H4	127 (10)	As2—O8—N ^{ix}	173.9 (3)
O6—N—H4	68 (10)	As2—O8—N ^{iv}	99.4 (2)
O7 ^{iv} —N—H4	124 (10)	N ^{ix} —O8—N ^{iv}	77.87 (12)
O3—N—H4	130 (10)	As2—O8—N ^{vii}	69.8 (2)
O8 ^v —N—H4	66 (10)	N ^{ix} —O8—N ^{vii}	108.5 (3)
O3 ⁱ —N—H4	74 (10)	N ^{iv} —O8—N ^{vii}	138.29 (17)

O4—N—H4	152 (10)	As2—O8—N	34.20 (18)
As2—N—H4	87 (10)	N ^{ix} —O8—N	139.75 (18)
As1 ⁱ —N—H4	90 (10)	N ^{iv} —O8—N	85.3 (2)
O6 ^{vi} —N—H4	62 (10)	N ^{vii} —O8—N	62.91 (12)
As1—N—H4	146 (10)	As2—O8—H9	94 (8)
H1—N—H4	116 (10)	N ^{ix} —O8—H9	80 (8)
H2—N—H4	104 (10)	N ^{iv} —O8—H9	39 (9)
H3—N—H4	96 (10)	N ^{vii} —O8—H9	100 (9)
O1—As1—O2	114.3 (3)	N—O8—H9	64 (8)
O1—As1—O3	109.7 (3)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N—H1 \cdots O4 ⁱⁱⁱ	0.89 (2)	2.36 (8)	3.082 (9)	138 (10)
N—H1 \cdots O7 ^{iv}	0.89 (2)	2.54 (9)	3.194 (10)	130 (9)
N—H4 \cdots O5 ⁱ	0.90 (2)	2.20 (7)	3.032 (11)	154 (14)
N—H3 \cdots O1 ⁱ	0.89 (2)	2.10 (4)	2.947 (9)	159 (9)
N—H2 \cdots O5	0.91 (2)	1.96 (2)	2.869 (10)	174 (7)
O3—H5 \cdots O1 ^{viii}	0.89 (2)	2.13 (15)	2.616 (7)	113 (12)
O3—H5 \cdots O3 ⁱⁱ	0.89 (2)	2.61 (11)	3.311 (12)	136 (13)
O6—H7 \cdots O2 ^{xi}	0.90 (2)	1.82 (10)	2.653 (9)	152 (19)
O4—H6 \cdots O1 ⁱ	0.89 (2)	1.77 (3)	2.650 (8)	170 (7)
O7—H8 \cdots O2 ^{xii}	0.89 (2)	1.72 (4)	2.568 (8)	157 (8)
O8—H9 \cdots O5 ^{iv}	0.89 (2)	1.78 (6)	2.590 (7)	150 (11)

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