



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

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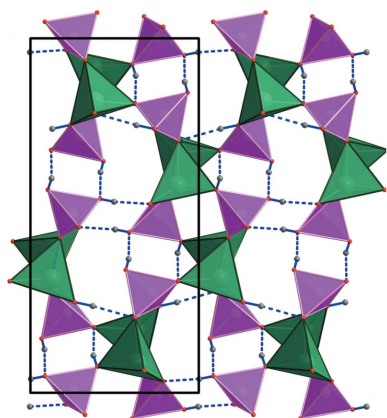
The crystal structures of caesium dihydrogen arsenate(V) bis[trihydrogen arsenate(V)],  $Cs(H_2AsO_4)(H_3AsO_4)_2$ , ammonium dihydrogen arsenate(V) trihydrogen arsenate(V),  $NH_4(H_2AsO_4)(H_3AsO_4)$ , and dilithium bis(dihydrogen phosphate),  $Li_2(H_2PO_4)_2$ , were solved from single-crystal X-ray 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).

|  | <b>Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub></b>   | <b>(NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)</b>    | <b>Li<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub></b> |
|--|---|--|--|
| Crystal data   |   |  |  |
| Chemical formula   | Cs(H <sub>2</sub> AsO <sub>4</sub> )(H <sub>3</sub> AsO <sub>4</sub> ) <sub>2</sub> | (NH <sub>4</sub> )(H <sub>2</sub> AsO <sub>4</sub> )(H <sub>3</sub> AsO <sub>4</sub> ) | Li <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> |
| $M_r$  | 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)                               |
| $\alpha, \beta, \gamma$ (°)  | 90, 90.91 (3), 90   | 90, 90, 90   | 90, 90.47 (3), 90  |
| $V$ (Å <sup>3</sup> )  | 1151.2 (4)  | 1536.1 (6)   | 650.4 (2)  |
| $Z$  | 4   | 8  | 4  |
| $\mu$ (mm <sup>-1</sup> )  | 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   |
| $R_{\text{int}}$   | 0.016   | 0.038  | 0.014  |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )                    | 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 <sup>-3</sup> ) | 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 Li<sub>4</sub>H(PO<sub>3</sub>)<sub>5</sub>, LiH<sub>2</sub>PO<sub>2</sub>, Li<sub>6</sub>(P<sub>6</sub>O<sub>18</sub>)(H<sub>2</sub>O)<sub>3</sub>, Li<sub>4</sub>P<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>, Li<sub>3</sub>(P<sub>3</sub>O<sub>9</sub>)(H<sub>2</sub>O)<sub>3</sub>, Li<sub>6</sub>(P<sub>6</sub>O<sub>18</sub>)(H<sub>2</sub>O)<sub>5</sub>, Li<sub>4</sub>(P<sub>4</sub>O<sub>12</sub>)(H<sub>2</sub>O)<sub>5</sub>, Li<sub>6</sub>(P<sub>6</sub>O<sub>18</sub>)(H<sub>2</sub>O)<sub>8.24</sub>, Li<sub>6</sub>(P<sub>6</sub>O<sub>18</sub>)(H<sub>2</sub>O)<sub>9.86</sub>, Li<sub>3</sub>PO<sub>4</sub> and Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.

Known caesium arsenates include CsAs<sub>3</sub>O<sub>8</sub> (Schwendtner & Kolitsch, 2007a), Cs<sub>3</sub>AsO<sub>4</sub> (Emmerling *et al.*, 2002), Cs<sub>2</sub>(HAsO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub> (Stöger & Weil, 2014), KDP-type Cs(H<sub>2</sub>AsO<sub>4</sub>) (Ferrari *et al.*, 1956) and CsH<sub>5</sub>(AsO<sub>4</sub>)<sub>2</sub> (Naili *et al.*, 2001). Ammonium arsenate compounds comprise (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>), for which a tetragonal KDP-type polymorph (Khan & Baur, 1972) and an orthorhombic low-temperature polymorph (Fukami, 1989) were reported, (NH<sub>4</sub>)<sub>2</sub>(HAsO<sub>4</sub>) (Weil, 2012) and (NH<sub>4</sub>)<sub>3</sub>(AsO<sub>4</sub>)(H<sub>2</sub>O)<sub>3</sub> (Hseu & Lu, 1977).

Compounds containing H<sub>3</sub>AsO<sub>4</sub> 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 H<sub>3</sub>AsO<sub>4</sub> group) and with known crystal structures are restricted to only seven representatives: CuH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> (Tran Qui & Chiadmi, 1986) and isotopic ZnH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> (Sure & Guse, 1989) (the O–H bonds were not clearly identified in the latter structure determination), RbH<sub>5</sub>(AsO<sub>4</sub>)<sub>2</sub> (Naili & Mhiri, 2001), CsH<sub>5</sub>(AsO<sub>4</sub>)<sub>2</sub> (Naili *et al.*, 2001), K<sub>4</sub>(SO<sub>4</sub>)(HSO<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>AsO<sub>4</sub>) (Amri *et al.*, 2007), Cs<sub>4</sub>(SeO<sub>4</sub>)(HSeO<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>AsO<sub>4</sub>) (Amri *et al.*, 2009) and isotopic Rb<sub>4</sub>(SO<sub>4</sub>)(HSO<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>AsO<sub>4</sub>) (Belhaj Salah *et al.*, 2018). (NH<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>AsO<sub>4</sub>)(SO<sub>4</sub>) (Boubia *et al.*, 1985) also con-

tains H<sub>3</sub>AsO<sub>4</sub> groups, but the H atoms were not located, and for CdH<sub>10</sub>(AsO<sub>4</sub>)<sub>4</sub> (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. NH<sub>4</sub>(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) was grown by hydrothermal methods ( $T = 493$  K, 7 d, Teflon-lined stainless steel autoclave) from a mixture of In<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>AsO<sub>4</sub>·0.5H<sub>2</sub>O in an approximate volume ratio of 1:10 and 10 drops of NH<sub>4</sub>(OH) (32%). No additional H<sub>2</sub>O was added. The reaction product was a solid mass of colourless intergrown crystals with less than 10 vol% of a yellow unidentified material. The NH<sub>4</sub>(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) crystals are stable in air.

Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub> formed as the secondary product from further reaction of hydrothermally grown CsAs<sub>3</sub>O<sub>8</sub> (Schwendtner & Kolitsch, 2007a). CsAs<sub>3</sub>O<sub>8</sub> contains AsO<sub>6</sub> groups, is highly hygroscopic and, at room temperature, decomposes to a highly acidic liquid in which rounded prismatic glassy colourless crystals of Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub> grew within a few weeks.

Li<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> was also a secondary product of a hydrothermal run ( $T = 493$  K, 7 d, Teflon-lined stainless steel autoclave) from a mixture of Li<sub>2</sub>CO<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, 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(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>.

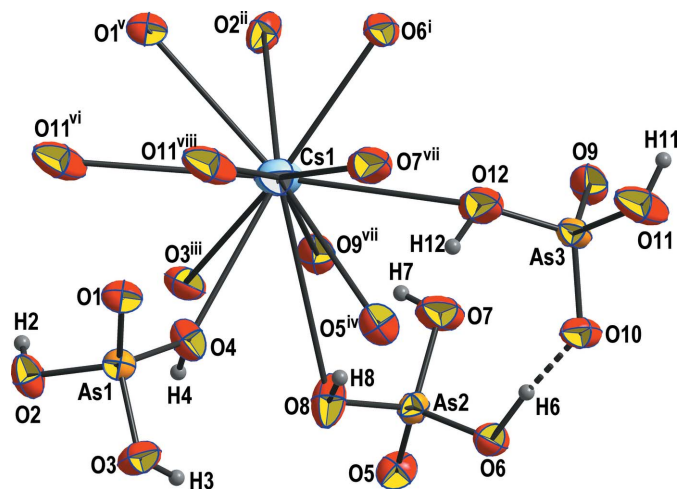
|                         |             |         |             |
|-------------------------|-------------|---------|-------------|
| Cs1—O6 <sup>i</sup>     | 3.1202 (17) | As1—O1  | 1.6437 (15) |
| Cs1—O2 <sup>ii</sup>    | 3.2184 (19) | As1—O2  | 1.6903 (17) |
| Cs1—O3 <sup>iii</sup>   | 3.2326 (19) | As1—O3  | 1.6970 (17) |
| Cs1—O4                  | 3.2469 (17) | As1—O4  | 1.7025 (16) |
| Cs1—O5 <sup>iv</sup>    | 3.2536 (18) | As2—O5  | 1.6390 (16) |
| Cs1—O1 <sup>v</sup>     | 3.3579 (17) | As2—O6  | 1.6874 (16) |
| Cs1—O11 <sup>vi</sup>   | 3.359 (2)   | As2—O7  | 1.6977 (19) |
| Cs1—O12                 | 3.478 (2)   | As2—O8  | 1.7004 (19) |
| Cs1—O9 <sup>vii</sup>   | 3.7056 (19) | As3—O9  | 1.6515 (16) |
| Cs1—O11 <sup>viii</sup> | 3.755 (3)   | As3—O10 | 1.6579 (17) |
| Cs1—O8                  | 3.844 (2)   | As3—O12 | 1.707 (2)   |
| Cs1—O7 <sup>vii</sup>   | 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 GaPO<sub>4</sub>. From the remaining acidic liquid of the synthesis, Li<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> 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. NH<sub>4</sub>(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) 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 NH<sub>4</sub>(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) recrystallized to pseudocubic  $\bar{I}42d$ -type (NH<sub>4</sub>)H<sub>2</sub>AsO<sub>4</sub> (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  $0.9 \pm 0.2$  Å, as was the O6–H6 bond in Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>. The O–H bonds in Li<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

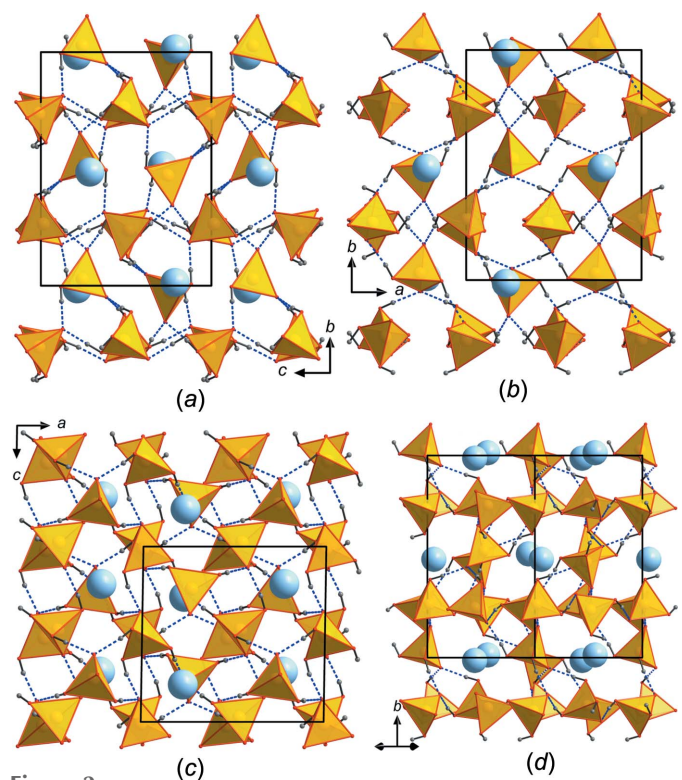


**Figure 1**  
The principal building unit of Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>, shown as displacement ellipsoids at the 70% probability level. The symmetry codes are as defined in Table 2.

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(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub> 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 H<sub>3</sub>AsO<sub>4</sub>-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 AsO<sub>4</sub> tetrahedra into a three-dimensional (3D) network (Figs. 2a–c). In the [101]



**Figure 2**  
Structural drawings of novel Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>, viewed along (a) *a*, (b) *c*, (c) *b* and (d) [101]. The unit cell is outlined. AsO<sub>4</sub> tetrahedra (yellow) are connected *via* multiple hydrogen bonds (blue) into a 3D network. The Cs<sup>+</sup> cations lie between the AsO<sub>4</sub> tetrahedra.

**Table 3**  
 Hydrogen-bond geometry (Å, °) for Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>.

| <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 <sup>viii</sup> | 0.83 (4)    | 1.70 (4)      | 2.524 (2)             | 171 (4)                 |
| O3—H3···O9 <sup>ix</sup>    | 0.79 (4)    | 1.76 (4)      | 2.553 (3)             | 172 (4)                 |
| O4—H4···O1 <sup>iii</sup>   | 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 <sup>vii</sup>   | 0.81 (4)    | 1.79 (4)      | 2.599 (3)             | 177 (4)                 |
| O11—H11···O1 <sup>vi</sup>  | 0.79 (4)    | 1.85 (4)      | 2.630 (3)             | 168 (4)                 |
| O8—H8···O5 <sup>iv</sup>    | 0.82 (4)    | 1.85 (4)      | 2.664 (2)             | 170 (4)                 |
| O12—H12···O5 <sup>iv</sup>  | 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)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ .

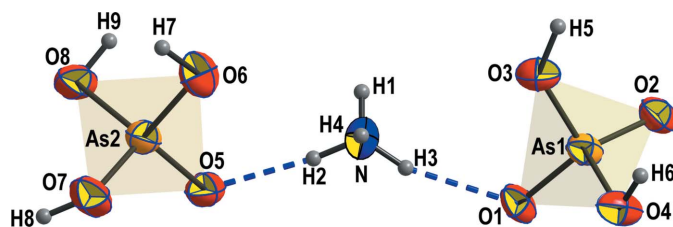
**Table 4**  
 Selected bond lengths (Å) for (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>).

|                     |            |                   |            |
|---------------------|------------|-------------------|------------|
| N—O5                | 2.869 (10) | N—O3 <sup>i</sup> | 3.283 (10) |
| N—O1 <sup>i</sup>   | 2.947 (9)  | As1—O1            | 1.648 (5)  |
| N—O5 <sup>i</sup>   | 3.032 (11) | As1—O2            | 1.662 (6)  |
| N—O2 <sup>ii</sup>  | 3.075 (9)  | As1—O3            | 1.705 (6)  |
| N—O4 <sup>iii</sup> | 3.082 (9)  | As1—O4            | 1.714 (5)  |
| N—O6                | 3.148 (10) | As2—O5            | 1.632 (6)  |
| N—O7 <sup>iv</sup>  | 3.194 (10) | As2—O8            | 1.692 (5)  |
| N—O3                | 3.216 (10) | As2—O7            | 1.693 (5)  |
| N—O8 <sup>v</sup>   | 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 AsO<sub>4</sub> tetrahedra in which the Cs atom is located (Fig. 2*d*).

The structure of (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) is homeotypic with that of Rb(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) (Naili & Mhiri, 2001); the Rb<sup>+</sup> cation is replaced by an NH<sub>4</sub><sup>+</sup> group providing additional hydrogen bonds to the atomic arrangement. This structure type is also closely related to that of CsH<sub>5</sub>(AsO<sub>4</sub>)<sub>2</sub> (Naili *et al.*, 2001), which can be seen as a distorted version of the Rb(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) structure type. The structure of (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) is built of individual, doubly or triply protonated AsO<sub>4</sub> tetrahedra that are connected *via* strong hydrogen bonds into a 3D network (Figs. 3, 4*a* and 4*b*). The NH<sub>4</sub><sup>+</sup> groups lie in voids and further reinforce the network *via* medium-to-weak strength hydrogen bonds. AsO<sub>4</sub> tetrahedra and NH<sub>4</sub><sup>+</sup> cations are arranged in layers perpendicular to *c* (Fig. 4). The NH<sub>4</sub><sup>+</sup> 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 AsO<sub>4</sub> groups are overbonded (5.08 and 5.13 v.u. for As1 and



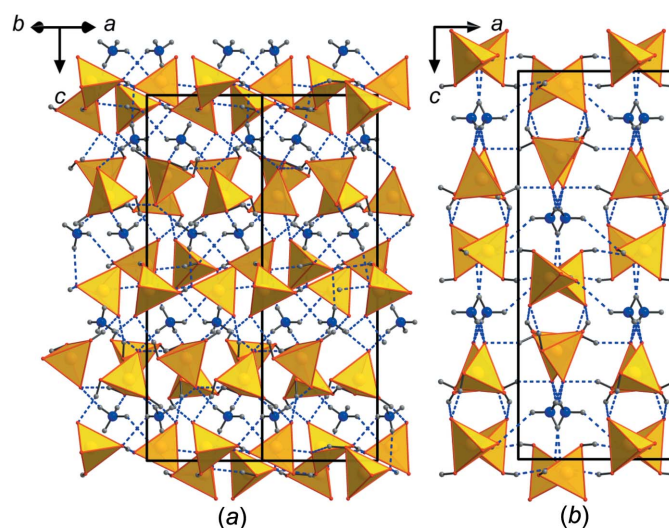
**Figure 3**  
 The principal building unit of (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>), shown as displacement ellipsoids at the 70% probability level. Hydrogen bonds are shown as blue dashed lines.

**Table 5**  
 Hydrogen-bond geometry (Å, °) for (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>).

| <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 <sup>iii</sup>   | 0.89 (2)    | 2.36 (8)      | 3.082 (9)             | 138 (10)                |
| N—H1···O7 <sup>iv</sup>    | 0.89 (2)    | 2.54 (9)      | 3.194 (10)            | 130 (9)                 |
| N—H4···O5 <sup>i</sup>     | 0.90 (2)    | 2.20 (7)      | 3.032 (11)            | 154 (14)                |
| N—H3···O1 <sup>i</sup>     | 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 <sup>vi</sup>   | 0.89 (2)    | 2.13 (15)     | 2.616 (7)             | 113 (12)                |
| O3—H5···O3 <sup>ii</sup>   | 0.89 (2)    | 2.61 (11)     | 3.311 (12)            | 136 (13)                |
| O6—H7···O2 <sup>vii</sup>  | 0.90 (2)    | 1.82 (10)     | 2.653 (9)             | 152 (19)                |
| O4—H6···O1 <sup>i</sup>    | 0.89 (2)    | 1.77 (3)      | 2.650 (8)             | 170 (7)                 |
| O7—H8···O2 <sup>viii</sup> | 0.89 (2)    | 1.72 (4)      | 2.568 (8)             | 157 (8)                 |
| O8—H9···O5 <sup>iv</sup>   | 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(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>) (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*<sup>+</sup>H<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> compounds [see compilation in Naili & Mhiri (2001)]. In (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>), 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 (NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>), viewed along (a) [110] and (b) *b*. The unit cell is outlined. AsO<sub>4</sub> tetrahedra (yellow) are connected *via* multiple hydrogen bonds (blue dashed lines) into a 3D network. AsO<sub>4</sub> tetrahedra and NH<sub>4</sub><sup>+</sup> cations are arranged in layers perpendicular to *c*. Additional hydrogen bonds of medium strength are provided by the NH<sub>4</sub><sup>+</sup> 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)       |

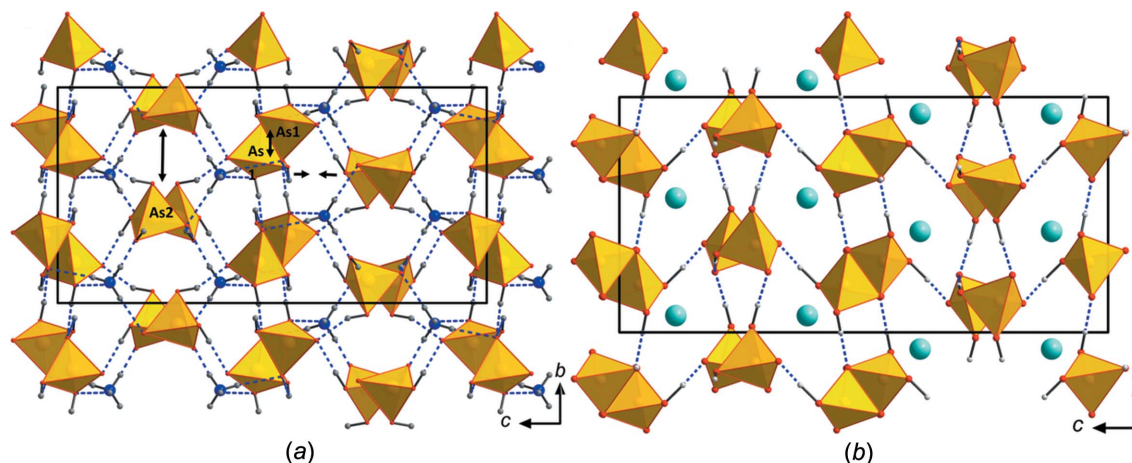
Symmetry codes: (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (vi)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $-x + 2, -y + 1, -z + 1$ ; (viii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ .

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

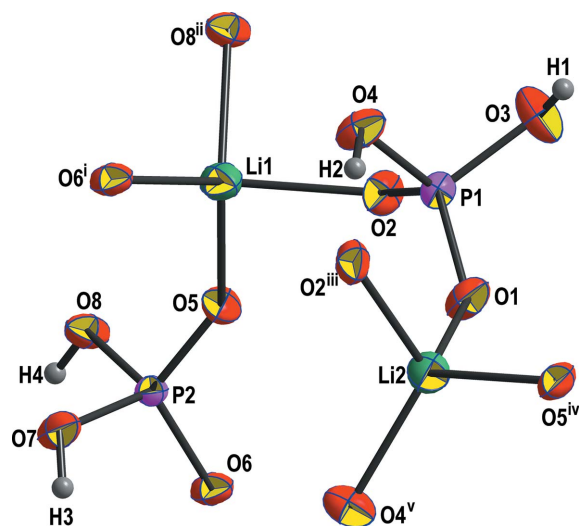
|                                      |           |                                    |            |
|--------------------------------------|-----------|------------------------------------|------------|
| $\text{Li}1-\text{O}5$               | 1.888 (2) | $\text{Li}2-\text{P}2^{\text{iv}}$ | 3.077 (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  $\text{NH}_4^+$  and  $\text{Rb}^+$  (the latter is slightly smaller), firstly, by the ability of the  $\text{NH}_4^+$  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  $\text{LiO}_4$  tetrahedra that share edges with adjacent  $\text{LiO}_4$  tetrahedra, thereby forming  $\text{Li}_2\text{O}_6$  dimers (Fig. 7b). Each corner of the  $\text{LiO}_4$  tetrahedra shares a corner with a  $\text{PO}_4$  tetrahedron, thus connecting the  $\text{Li}_2\text{O}_6$  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  $\text{LiO}_4$  tetrahedra share corners, thus forming chains that are connected by the  $\text{PO}_4$  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).

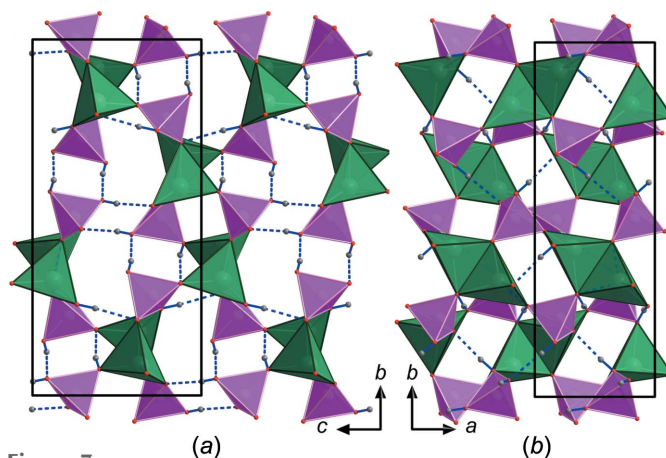
bond lengths. This is also reflected by the nearly ideal BVSS (Gagné & Hawthorne, 2015) of 1.01 and 1.00 v.u. for Li1 and Li2, respectively, and 4.98 and 5.00 v.u. for P1 and P2, respectively. The most underbonded O atoms (O3, O4, O7 and O8, with BVSSs of 1.16–1.37 v.u.) form strong-to-medium hydrogen bonds (Table 6). A comparison of the X-ray densities of monoclinic  $Li_2(H_2PO_4)_2$  ( $2.123 \text{ kg m}^{-3}$ ) and its orthorhombic dimorph  $LiH_2PO_4$  (Catti & Ivaldi, 1978) ( $2.09 \text{ kg m}^{-3}$ ) 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

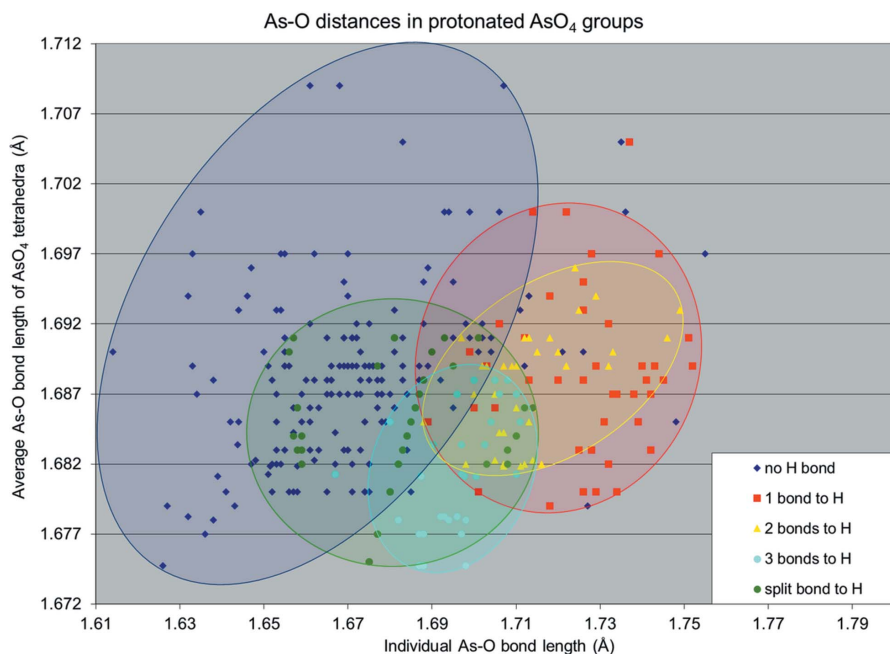
Several statistical analyses of bond lengths in  $As^{5+}O_4$  polyhedra have been published recently. Gagné & Hawthorne (2018a) reported average As—O bond lengths of 1.687 (27) Å in  $AsO_4$  and 1.830 (28) Å in  $AsO_6$  groups, derived from 508 and 13 polyhedra, respectively. Schwendtner (2008) found 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

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## 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)] (CsH<sub>2</sub>AsO<sub>4</sub>H<sub>3</sub>AsO<sub>4</sub>)

#### Crystal data

Cs(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)<sub>2</sub>

$M_r = 557.73$

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) Å<sup>3</sup>

$Z = 4$

$F(000) = 1032$

$D_x = 3.218$  Mg m<sup>-3</sup>

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

Cell parameters from 4360 reflections

$\theta = 2.7$ – $32.6$ °

$\mu = 11.83$  mm<sup>-1</sup>

$T = 293$  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

$\varphi$  and  $\omega$  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<sup>-3</sup>

$\Delta\rho_{\min} = -1.60$  e Å<sup>-3</sup>

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 ( $\text{\AA}^2$ )*

|     | <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 ( $\text{\AA}^2$ )*

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| 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 <sup>i</sup>                     | 3.1202 (17) | Cs1—H3 <sup>iii</sup>                   | 3.25 (4)    |
| Cs1—O2 <sup>ii</sup>                    | 3.2184 (19) | Cs1—H6 <sup>i</sup>                     | 3.43 (4)    |
| Cs1—O3 <sup>iii</sup>                   | 3.2326 (19) | As1—O1                                  | 1.6437 (15) |
| Cs1—O4                                  | 3.2469 (17) | As1—O2                                  | 1.6903 (17) |
| Cs1—O5 <sup>iv</sup>                    | 3.2536 (18) | As1—O3                                  | 1.6970 (17) |
| Cs1—O1 <sup>v</sup>                     | 3.3579 (17) | As1—O4                                  | 1.7025 (16) |
| Cs1—O11 <sup>vi</sup>                   | 3.359 (2)   | As2—O5                                  | 1.6390 (16) |
| Cs1—O12                                 | 3.478 (2)   | As2—O6                                  | 1.6874 (16) |
| Cs1—O9 <sup>vii</sup>                   | 3.7056 (19) | As2—O7                                  | 1.6977 (19) |
| Cs1—O11 <sup>viii</sup>                 | 3.755 (3)   | As2—O8                                  | 1.7004 (19) |
| Cs1—O8                                  | 3.844 (2)   | As3—O9                                  | 1.6515 (16) |
| Cs1—O7 <sup>vii</sup>                   | 3.924 (3)   | As3—O10                                 | 1.6579 (17) |
| Cs1—O12 <sup>vi</sup>                   | 4.028 (3)   | As3—O12                                 | 1.707 (2)   |
| Cs1—O7                                  | 4.077 (3)   | As3—O11                                 | 1.7104 (19) |
| Cs1—O3 <sup>ii</sup>                    | 4.103 (2)   | O2—H2                                   | 0.83 (4)    |
| Cs1—O10 <sup>i</sup>                    | 4.2239 (19) | O3—H3                                   | 0.79 (4)    |
| Cs1—As1 <sup>ii</sup>                   | 4.3298 (9)  | O4—H4                                   | 0.92 (3)    |
| Cs1—As3 <sup>vi</sup>                   | 4.3913 (10) | O6—H6                                   | 0.910 (18)  |
| Cs1—As1 <sup>v</sup>                    | 4.5175 (9)  | O7—H7                                   | 0.81 (4)    |
| Cs1—O2 <sup>v</sup>                     | 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 <sup>ii</sup>                    | 3.45 (4)    |   |             |
| O6 <sup>i</sup> —Cs1—O2 <sup>ii</sup>   | 70.42 (5)   | As1 <sup>ii</sup> —Cs1—H12              | 142.7 (7)   |
| O6 <sup>i</sup> —Cs1—O3 <sup>iii</sup>  | 154.40 (5)  | As3 <sup>vi</sup> —Cs1—H12              | 74.4 (6)    |
| O2 <sup>ii</sup> —Cs1—O3 <sup>iii</sup> | 85.00 (5)   | As1 <sup>v</sup> —Cs1—H12               | 124.7 (6)   |
| O6 <sup>i</sup> —Cs1—O4                 | 143.71 (4)  | O2 <sup>v</sup> —Cs1—H12                | 103.5 (6)   |
| O2 <sup>ii</sup> —Cs1—O4                | 140.79 (5)  | H8—Cs1—H12                              | 55.5 (9)    |
| O3 <sup>iii</sup> —Cs1—O4               | 61.72 (4)   | O6 <sup>i</sup> —Cs1—H2 <sup>ii</sup>   | 57.7 (6)    |
| O6 <sup>i</sup> —Cs1—O5 <sup>iv</sup>   | 100.47 (5)  | O2 <sup>ii</sup> —Cs1—H2 <sup>ii</sup>  | 13.8 (6)    |
| O2 <sup>ii</sup> —Cs1—O5 <sup>iv</sup>  | 153.62 (4)  | O3 <sup>iii</sup> —Cs1—H2 <sup>ii</sup> | 98.4 (6)    |
| O3 <sup>iii</sup> —Cs1—O5 <sup>iv</sup> | 98.54 (5)   | O4—Cs1—H2 <sup>ii</sup>                 | 149.2 (7)   |
| O4—Cs1—O5 <sup>iv</sup>                 | 59.07 (4)   | O5 <sup>iv</sup> —Cs1—H2 <sup>ii</sup>  | 151.5 (7)   |
| O6 <sup>i</sup> —Cs1—O1 <sup>v</sup>    | 74.39 (4)   | O1 <sup>v</sup> —Cs1—H2 <sup>ii</sup>   | 53.0 (7)    |
| O2 <sup>ii</sup> —Cs1—O1 <sup>v</sup>   | 58.54 (4)   | O11 <sup>vi</sup> —Cs1—H2 <sup>ii</sup> | 111.7 (6)   |

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

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

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

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

|                              |           |   |             |
|------------------------------|-----------|---|-------------|
| O3 <sup>ii</sup> —Cs1—H8     | 114.7 (6) | As3—O10—Cs1 <sup>vi</sup>                 | 59.93 (5)   |
| O10 <sup>i</sup> —Cs1—H8     | 156.5 (6) | Cs1 <sup>x</sup> —O10—Cs1 <sup>vi</sup>   | 111.15 (3)  |
| As1 <sup>ii</sup> —Cs1—H8    | 134.8 (6) | As3—O10—Cs1 <sup>vii</sup>                | 78.77 (6)   |
| As3 <sup>vi</sup> —Cs1—H8    | 99.2 (6)  | Cs1 <sup>x</sup> —O10—Cs1 <sup>vii</sup>  | 110.89 (3)  |
| As1 <sup>v</sup> —Cs1—H8     | 154.2 (6) | Cs1 <sup>vi</sup> —O10—Cs1 <sup>vii</sup> | 137.79 (4)  |
| O2 <sup>v</sup> —Cs1—H8      | 148.0 (6) | As3—O10—Cs1 <sup>xi</sup>                 | 72.57 (6)   |
| O6 <sup>i</sup> —Cs1—H12     | 72.2 (7)  | Cs1 <sup>x</sup> —O10—Cs1 <sup>xi</sup>   | 113.62 (3)  |
| O2 <sup>ii</sup> —Cs1—H12    | 123.9 (7) | Cs1 <sup>vi</sup> —O10—Cs1 <sup>xi</sup>  | 76.59 (3)   |
| O3 <sup>iii</sup> —Cs1—H12   | 118.9 (6) | Cs1 <sup>vii</sup> —O10—Cs1 <sup>xi</sup> | 83.52 (4)   |
| O4—Cs1—H12                   | 91.9 (7)  | As3—O11—Cs1 <sup>vi</sup>                 | 116.21 (11) |
| O5 <sup>iv</sup> —Cs1—H12    | 32.8 (7)  | As3—O11—Cs1 <sup>xi</sup>                 | 119.34 (11) |
| O1 <sup>v</sup> —Cs1—H12     | 141.8 (6) | Cs1 <sup>vi</sup> —O11—Cs1 <sup>xi</sup>  | 121.90 (6)  |
| O11 <sup>vi</sup> —Cs1—H12   | 91.0 (6)  | As3—O11—H11                               | 115 (3)     |
| O12—Cs1—H12                  | 13.3 (7)  | Cs1 <sup>vi</sup> —O11—H11                | 102 (3)     |
| O9 <sup>vii</sup> —Cs1—H12   | 93.7 (6)  | Cs1 <sup>xi</sup> —O11—H11                | 68 (3)      |
| O11 <sup>viii</sup> —Cs1—H12 | 145.1 (6) | As3—O12—Cs1                               | 142.50 (11) |
| O8—Cs1—H12                   | 63.9 (6)  | As3—O12—Cs1 <sup>vi</sup>                 | 90.58 (9)   |
| O7 <sup>vii</sup> —Cs1—H12   | 66.1 (6)  | Cs1—O12—Cs1 <sup>vi</sup>                 | 126.73 (6)  |
| O12 <sup>vi</sup> —Cs1—H12   | 51.9 (6)  | As3—O12—H12                               | 110 (3)     |
| O7—Cs1—H12                   | 55.3 (6)  | Cs1—O12—H12                               | 68 (3)      |
| O3 <sup>ii</sup> —Cs1—H12    | 149.4 (6) | Cs1 <sup>vi</sup> —O12—H12                | 95 (3)      |
| O10 <sup>i</sup> —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 <sup>viii</sup> | 0.83 (4) | 1.70 (4)    | 2.524 (2)   | 171 (4)       |
| O3—H3 $\cdots$ O9 <sup>x</sup>     | 0.79 (4) | 1.76 (4)    | 2.553 (3)   | 172 (4)       |
| O4—H4 $\cdots$ O1 <sup>iii</sup>   | 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 <sup>vii</sup>   | 0.81 (4) | 1.79 (4)    | 2.599 (3)   | 177 (4)       |
| O11—H11 $\cdots$ O1 <sup>vi</sup>  | 0.79 (4) | 1.85 (4)    | 2.630 (3)   | 168 (4)       |
| O8—H8 $\cdots$ O5 <sup>iv</sup>    | 0.82 (4) | 1.85 (4)    | 2.664 (2)   | 170 (4)       |
| O12—H12 $\cdots$ O5 <sup>iv</sup>  | 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) (Li<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

##### Crystal data

Li<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>

$M_r = 207.85$

Monoclinic,  $P2_1/n$

$a = 5.400$  (1)  $\text{\AA}$

$b = 15.927$  (3)  $\text{\AA}$

$c = 7.562$  (2)  $\text{\AA}$

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

$V = 650.4$  (2)  $\text{\AA}^3$

$Z = 4$

$F(000) = 416$

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

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

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

$\varphi$  and  $\omega$  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 ( $\text{\AA}^2$ )*

|     | <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 ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|-------------|--------------|--------------|
| 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 ( $\text{\AA}$ ,  $^\circ$ )

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

|   |             |                            |            |
|---|-------------|----------------------------|------------|
| O1—Li2—O4 <sup>v</sup>                  | 106.56 (10) | P1—O1—Li2                  | 133.78 (8) |
| O5 <sup>iv</sup> —Li2—O2 <sup>iv</sup>  | 95.90 (9)   | P1—O2—Li2 <sup>iii</sup>   | 133.57 (8) |
| O1—Li2—O2 <sup>iv</sup>                 | 105.81 (10) | P1—O2—Li1                  | 129.67 (8) |
| O4 <sup>v</sup> —Li2—O2 <sup>iv</sup>   | 118.91 (11) | Li2 <sup>iii</sup> —O2—Li1 | 81.02 (8)  |
| O5 <sup>iv</sup> —Li2—Li1 <sup>iv</sup> | 46.19 (7)   | P1—O3—H1                   | 115.4 (17) |
| O1—Li2—Li1 <sup>iv</sup>                | 108.00 (10) | P1—O4—Li2 <sup>vii</sup>   | 129.92 (8) |
| O4 <sup>v</sup> —Li2—Li1 <sup>iv</sup>  | 145.44 (11) | P1—O4—H2                   | 108.9 (16) |
| O2 <sup>iv</sup> —Li2—Li1 <sup>iv</sup> | 50.68 (7)   | Li2 <sup>vii</sup> —O4—H2  | 121.0 (16) |
| O5 <sup>iv</sup> —Li2—P2 <sup>iv</sup>  | 22.43 (4)   | P2—O5—Li1                  | 144.45 (8) |
| O1—Li2—P2 <sup>iv</sup>                 | 106.59 (8)  | P2—O5—Li2 <sup>iii</sup>   | 128.24 (8) |
| O4 <sup>v</sup> —Li2—P2 <sup>iv</sup>   | 101.01 (8)  | Li1—O5—Li2 <sup>iii</sup>  | 86.62 (9)  |
| O2 <sup>iv</sup> —Li2—P2 <sup>iv</sup>  | 117.05 (8)  | P2—O6—Li1 <sup>vi</sup>    | 127.66 (8) |
| Li1 <sup>iv</sup> —Li2—P2 <sup>iv</sup> | 68.47 (6)   | P2—O7—H3                   | 116 (2)    |
| O1—P1—O2                                | 116.61 (5)  | P2—O8—Li1 <sup>ii</sup>    | 131.07 (8) |
| O1—P1—O3                                | 112.58 (5)  | P2—O8—H4                   | 111.6 (17) |
| O2—P1—O3                                | 104.53 (5)  | Li1 <sup>ii</sup> —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 <sup>viii</sup> | 0.77 (2) | 1.91 (2)    | 2.6769 (12) | 171 (2)       |
| O4—H2 $\cdots$ O2 <sup>iv</sup>   | 0.84 (2) | 1.99 (2)    | 2.8292 (14) | 176 (2)       |
| O7—H3 $\cdots$ O6 <sup>ix</sup>   | 0.73 (2) | 1.79 (2)    | 2.5210 (13) | 172 (3)       |
| O8—H4 $\cdots$ O1 <sup>x</sup>    | 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) (NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub>H<sub>3</sub>AsO<sub>4</sub>)

##### Crystal data

(NH<sub>4</sub>)(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>3</sub>AsO<sub>4</sub>)

$M_r = 300.92$

Orthorhombic, *Pbca*

$a = 7.943$  (2)  $\text{\AA}$

$b = 9.855$  (2)  $\text{\AA}$

$c = 19.623$  (4)  $\text{\AA}$

$V = 1536.1$  (6)  $\text{\AA}^3$

$Z = 8$

$F(000) = 1168$

##### Data collection

Nonius KappaCCD single-crystal four-circle diffractometer

Radiation source: fine-focus sealed tube

$\varphi$  and  $\omega$  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<sup>-3</sup>

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

Cell parameters from 793 reflections

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

$\mu = 8.71$  mm<sup>-1</sup>

$T = 293$  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),

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

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 ( $\text{\AA}^2$ )

|     | 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 ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|-----|------------|------------|------------|-------------|------------|-------------|
| 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 <sup>i</sup>                     | 2.947 (9)  | N—H4                                  | 0.90 (2)    |
| N—O5 <sup>i</sup>                     | 3.032 (11) | As1—O1                                | 1.648 (5)   |
| N—O2 <sup>ii</sup>                    | 3.075 (9)  | As1—O2                                | 1.662 (6)   |
| N—O4 <sup>iii</sup>                   | 3.082 (9)  | As1—O3                                | 1.705 (6)   |
| N—O6                                  | 3.148 (10) | As1—O4                                | 1.714 (5)   |
| N—O7 <sup>iv</sup>                    | 3.194 (10) | As2—O5                                | 1.632 (6)   |
| N—O3                                  | 3.216 (10) | As2—O8                                | 1.692 (5)   |
| N—O8 <sup>v</sup>                     | 3.272 (9)  | As2—O7                                | 1.693 (5)   |
| N—O3 <sup>i</sup>                     | 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 <sup>i</sup>                    | 3.755 (8)  | O4—H6                                 | 0.89 (2)    |
| N—O6 <sup>vi</sup>                    | 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 <sup>i</sup>                  | 130.2 (3)  | O2—As1—O3                             | 111.4 (3)   |
| O5—N—O5 <sup>i</sup>                  | 114.3 (3)  | O1—As1—O4                             | 106.0 (2)   |
| O1 <sup>i</sup> —N—O5 <sup>i</sup>    | 107.3 (3)  | O2—As1—O4                             | 111.9 (3)   |
| O5—N—O2 <sup>ii</sup>                 | 92.1 (2)   | O3—As1—O4                             | 102.8 (3)   |
| O1 <sup>i</sup> —N—O2 <sup>ii</sup>   | 70.0 (2)   | O1—As1—N <sup>vii</sup>               | 48.9 (2)    |
| O5 <sup>i</sup> —N—O2 <sup>ii</sup>   | 79.0 (2)   | O2—As1—N <sup>vii</sup>               | 135.4 (2)   |
| O5—N—O4 <sup>iii</sup>                | 116.1 (3)  | O3—As1—N <sup>vii</sup>               | 60.9 (2)    |
| O1 <sup>i</sup> —N—O4 <sup>iii</sup>  | 71.4 (2)   | O4—As1—N <sup>vii</sup>               | 112.6 (2)   |
| O5 <sup>i</sup> —N—O4 <sup>iii</sup>  | 109.4 (3)  | O1—As1—N                              | 114.9 (2)   |
| O2 <sup>ii</sup> —N—O4 <sup>iii</sup> | 141.2 (3)  | O2—As1—N                              | 130.3 (2)   |
| O5—N—O6                               | 52.6 (2)   | O3—As1—N                              | 43.6 (2)    |
| O1 <sup>i</sup> —N—O6                 | 173.6 (4)  | O4—As1—N                              | 59.5 (2)    |
| O5 <sup>i</sup> —N—O6                 | 67.3 (2)   | N <sup>vii</sup> —As1—N               | 77.08 (15)  |
| O2 <sup>ii</sup> —N—O6                | 105.0 (3)  | O1—As1—N <sup>ii</sup>                | 124.9 (2)   |
| O4 <sup>iii</sup> —N—O6               | 113.3 (3)  | O2—As1—N <sup>ii</sup>                | 31.2 (2)    |
| O5—N—O7 <sup>iv</sup>                 | 60.4 (2)   | O3—As1—N <sup>ii</sup>                | 80.4 (2)    |
| O1 <sup>i</sup> —N—O7 <sup>iv</sup>   | 124.2 (3)  | O4—As1—N <sup>ii</sup>                | 124.9 (2)   |
| O5 <sup>i</sup> —N—O7 <sup>iv</sup>   | 113.6 (3)  | N <sup>vii</sup> —As1—N <sup>ii</sup> | 116.13 (17) |
| O2 <sup>ii</sup> —N—O7 <sup>iv</sup>  | 152.3 (3)  | N—As1—N <sup>ii</sup>                 | 108.59 (12) |

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

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

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



|                        |           |                         |             |
|------------------------|-----------|-------------------------|-------------|
| O4—N—H4                | 152 (10)  | As2—O8—N                | 34.20 (18)  |
| As2—N—H4               | 87 (10)   | N <sup>ix</sup> —O8—N   | 139.75 (18) |
| As1 <sup>i</sup> —N—H4 | 90 (10)   | N <sup>iv</sup> —O8—N   | 85.3 (2)    |
| O6 <sup>vi</sup> —N—H4 | 62 (10)   | N <sup>vii</sup> —O8—N  | 62.91 (12)  |
| As1—N—H4               | 146 (10)  | As2—O8—H9               | 94 (8)      |
| H1—N—H4                | 116 (10)  | N <sup>ix</sup> —O8—H9  | 80 (8)      |
| H2—N—H4                | 104 (10)  | N <sup>iv</sup> —O8—H9  | 39 (9)      |
| H3—N—H4                | 96 (10)   | N <sup>vii</sup> —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 (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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N—H1 $\cdots$ O4 <sup>iii</sup>   | 0.89 (2)    | 2.36 (8)            | 3.082 (9)                  | 138 (10)                      |
| N—H1 $\cdots$ O7 <sup>iv</sup>    | 0.89 (2)    | 2.54 (9)            | 3.194 (10)                 | 130 (9)                       |
| N—H4 $\cdots$ O5 <sup>i</sup>     | 0.90 (2)    | 2.20 (7)            | 3.032 (11)                 | 154 (14)                      |
| N—H3 $\cdots$ O1 <sup>i</sup>     | 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 <sup>viii</sup> | 0.89 (2)    | 2.13 (15)           | 2.616 (7)                  | 113 (12)                      |
| O3—H5 $\cdots$ O3 <sup>ii</sup>   | 0.89 (2)    | 2.61 (11)           | 3.311 (12)                 | 136 (13)                      |
| O6—H7 $\cdots$ O2 <sup>xi</sup>   | 0.90 (2)    | 1.82 (10)           | 2.653 (9)                  | 152 (19)                      |
| O4—H6 $\cdots$ O1 <sup>i</sup>    | 0.89 (2)    | 1.77 (3)            | 2.650 (8)                  | 170 (7)                       |
| O7—H8 $\cdots$ O2 <sup>xii</sup>  | 0.89 (2)    | 1.72 (4)            | 2.568 (8)                  | 157 (8)                       |
| O8—H9 $\cdots$ O5 <sup>iv</sup>   | 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)  $x, -y+1/2, z-1/2$ .