

CsAl(H₂AsO₄)₂(HAsO₄): a new monoclinic protonated arsenate with decorated kröhnkite-like chains

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The crystal structure of hydrothermally synthesized caesium aluminium bis[dihydrogen arsenate(V)] hydrogen arsenate(V), CsAl(H₂AsO₄)₂(HAsO₄), was determined from single-crystal X-ray diffraction data collected at room temperature. The compound represents a new structure type that is characterized by decorated kröhnkite-like [100] chains of corner-sharing AlO₆ octahedra and AsO₄ tetrahedra. Ten-coordinated Cs atoms are situated between the chains, which are interconnected by five different hydrogen bonds [O...O = 2.569 (4)–2.978 (4) Å]. All atoms are in general positions. CsAl(H₂AsO₄)₂(HAsO₄) is very closely related to CsGa(H_{1.5}AsO₄)₂(H₂AsO₄) and isotypic CsCr(H_{1.5}AsO₄)₂(H₂AsO₄).

Comment

Arsenates, like phosphates and silicates, tend to form tetrahedral–octahedral framework structures with potentially interesting properties, such as ion conductivity, ion exchange and catalytic properties. The system M^I – M^{III} –As–O–H (M^I = Li, Na, K, Rb, Cs, Ag, Tl, NH₄ and H₃O; M^{III} = Al, Ga, In, Sc, Cr and Fe) is currently being studied closely by the authors to extend the knowledge on possible new arsenates and structure types. A large number of novel structure types and new compounds has been prepared and structurally characterized so far (Kolitsch, 2004; Kolitsch & Schwendtner, 2004, 2005; Schwendtner & Kolitsch, 2004*a,b*, 2005*a,b,c*, 2007*a,b*; Baran *et al.*, 2007; Schwendtner, 2006; Schwendtner *et al.*, 2006*a,b*).

The new title compound, CsAl(H₂AsO₄)₂(HAsO₄), is monoclinic (space group *Cc*) and represents a new chain-based structure type, very closely related to CsGa(H_{1.5}AsO₄)₂(H₂AsO₄) and isotypic CsCr(H_{1.5}AsO₄)₂(H₂AsO₄) (Schwendtner & Kolitsch, 2005*a*). The asymmetric unit contains 22 atoms, all of which lie in general positions. Atom Al1 is octahedrally coordinated (mean Al1–O = 1.904 Å; Table 1) and corner-linked to six AsO₄ tetrahedra to form decorated kröhnkite-like chains (Kolitsch & Fleck, 2006, and references therein) running parallel to [100] (Fig. 1). Ten-coordinated Cs1 atoms (mean Cs1–O = 3.254 Å) lie between these chains. All

three crystallographically different AsO₄ tetrahedra are protonated and highly distorted. The As–OH bonds are considerably elongated compared with the As–O bonds, which is typical for protonated AsO₄ tetrahedra (Ferraris, 1970; Ferraris & Ivaldi, 1984). The mean As–O bond lengths for the three AsO₄ tetrahedra range from 1.689 to 1.690 Å,

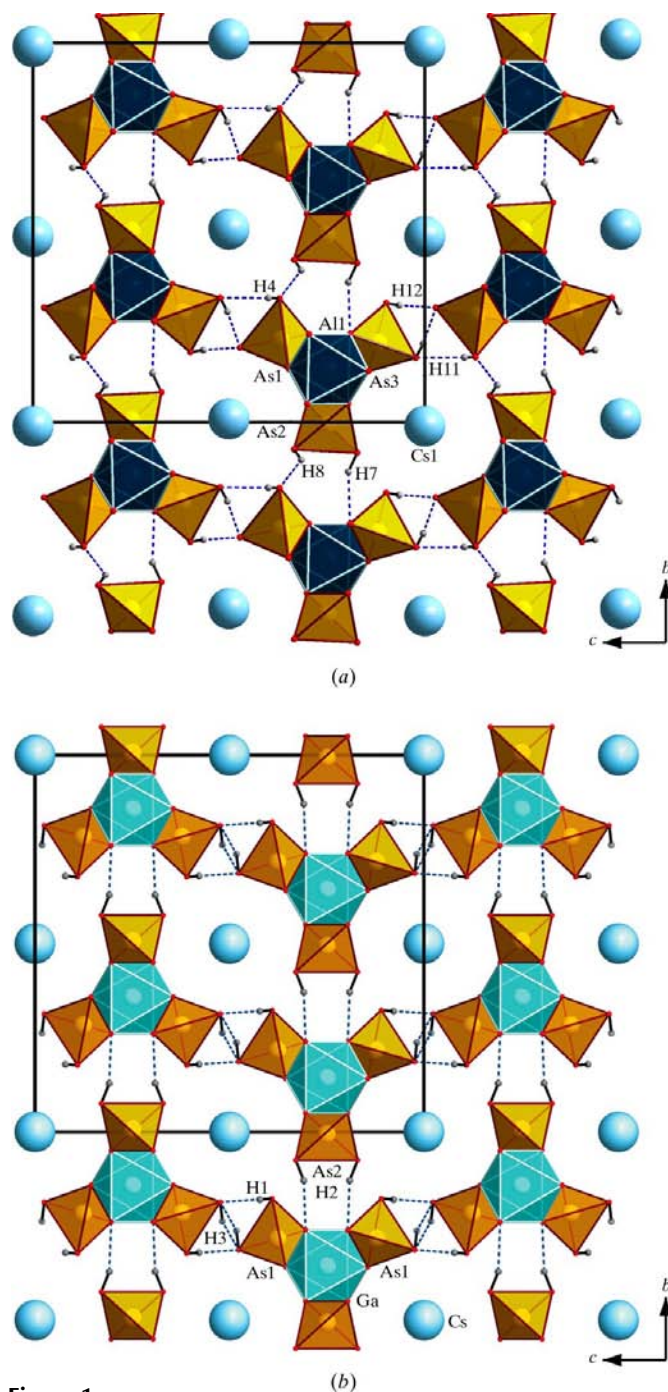


Figure 1
(a) A view of CsAl(H₂AsO₄)₂(HAsO₄) along [100]. Decorated kröhnkite-like chains run parallel to [100] and are connected through five different hydrogen bonds. The unit cell is outlined. (b) A view of CsGa(H_{1.5}AsO₄)₂(H₂AsO₄) (Schwendtner & Kolitsch, 2005*a*) along [100]. The main difference in comparison with (a) can be seen in the hydrogen bonds, the slight tilting of the AsO₄ tetrahedra and the location of the Cs atoms.

which are considerably longer than the average length for AsO_4 tetrahedra of 1.682 Å (Baur, 1981) as a result of protonation. As_3O_4 is doubly protonated and is involved in one strong $[\text{O}12 \cdots \text{O}3^{\text{v}} = 2.641(4) \text{ Å}]$; see Table 2 for symmetry codes] and one very strong hydrogen bond $[\text{O}11 \cdots \text{O}3^{\text{viii}} = 2.569(4) \text{ Å}]$. As_2O_4 is also doubly protonated with two medium-strength hydrogen bonds $[\text{O}8 \cdots \text{O}4^{\text{vii}} = 2.791(4) \text{ Å}$ and $\text{O}7 \cdots \text{O}10^{\text{i}} = 2.801(4) \text{ Å}]$, whereas As_1O_4 is only involved in one weak hydrogen bond $[\text{O}4 \cdots \text{O}11^{\text{vi}} = 2.978(4) \text{ Å}]$. The hydrogen bond between O11 and O3 is strongly disordered between the two O atoms. Bond-valence calculations suggest that both atoms act as donor and as

acceptor, since both atoms are highly underbonded (1.35 and 1.25 valence units for atoms O3 and O11, respectively). The longer As—O bond length to O11 and the smaller bond valence may indicate that the H atom is located on a position closer to the O11 atom, at least statistically, and has therefore been attached to O11 in the refinement process.

Bond-valence sums for all atoms were calculated using the bond-valence parameters from Brese & O'Keeffe (1991) for Al and from Brown & Altermatt (1985) for As and Cs. They are 1.08 (Cs1), 3.03 (Al1), 4.93 (As1 and As2), 4.94 (As3), 1.95 (O1), 1.80 (O2), 1.35 (O3), 1.17 (O4), 1.91 (O5), 1.89 (O6), 1.30 (O7), 1.27 (O8), 1.96 (O9), 1.76 (O10), 1.25 (O11) and 1.30 (O12) valence units. For the cations they are close to the ideal valences. The low sums for O3, O4, O7, O8 and O12 demonstrate that these belong to OH groups. The hydrogen bonds donated by the OH groups are accepted by O3, O4, O10 and O11 (Table 2).

The similarities between $\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HASO}_4)$ and $\text{Cs}M^{\text{III}}(\text{H}_{1.5}\text{AsO}_4)_2(\text{H}_2\text{AsO}_4)$ ($M^{\text{III}} = \text{Ga}$ and Cr ; $C2/c$; Schwendtner & Kolitsch, 2005a) are striking. Firstly, they have very similar unit-cell parameters [$a = 4.634(1)$, $4.714(1)$ and $4.744(1) \text{ Å}$; $b = 14.672(3)$, $14.674(3)$ and $14.625(3) \text{ Å}$; $c = 15.143(3)$, $15.162(3)$ and $15.127(3) \text{ Å}$; $\beta = 93.11(3)$, $93.31(3)$ and $93.48(3)^\circ$; and $V = 1028.7(4)$, $1047.1(4)$ and $1047.6(4) \text{ Å}^3$ for the CsAl, CsGa and CsCr compounds, respectively]. The Cc and $C2/c$ structure types both contain decorated kröhnkite-like chains running parallel to $[100]$. Owing to the smaller size of the Al atom compared with Cr or Ga, the structure is distorted, which results in a loss of the twofold axis. Polyhedra As_1O_4 (singly protonated) and As_3O_4 (doubly protonated) in the title compound are crystallographically equivalent to the As_1O_4 polyhedra (1.5 times protonated) in the CsGa and CsCr compounds. The formerly symmetry-restricted split double-well H-atom position in the $C2/c$ -type is not clearly detectable, but has probably now shifted towards As3 in the Cc -type (compare Figs. 1 and 2). Another difference concerns the doubly protonated As_2O_4 groups in both structure types. In the $C2/c$ -type structure, As2

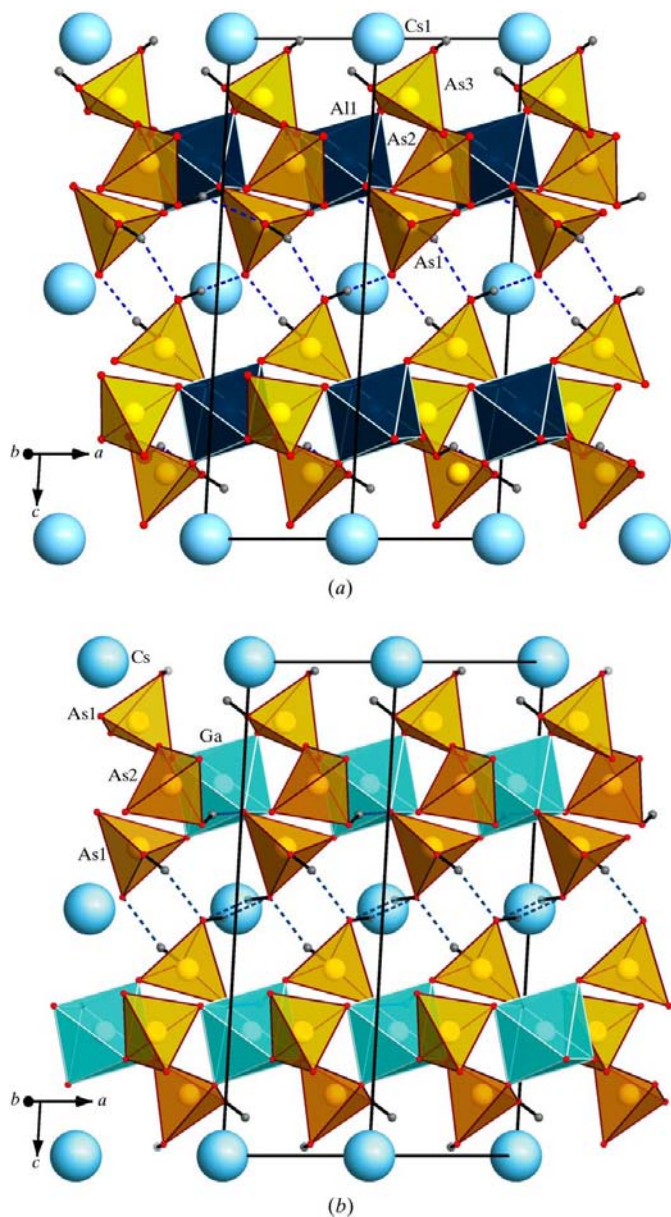


Figure 2
(a) A view of $\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HASO}_4)$ along $[110]$. Decorated kröhnkite-like chains run parallel to $[100]$ and are connected through five different hydrogen bonds. The unit cell is outlined. (b) A view of $\text{CsGa}(\text{H}_{1.5}\text{AsO}_4)_2(\text{H}_2\text{AsO}_4)$ (Schwendtner & Kolitsch, 2005a) along $[110]$. Decorated kröhnkite-like chains run parallel to $[100]$.

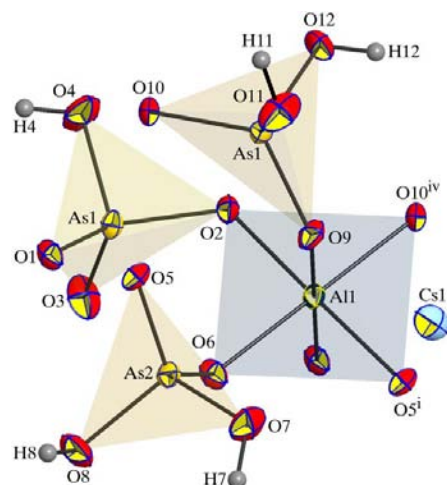


Figure 3
Displacement ellipsoid drawing of $\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HASO}_4)$ at the 70% probability level. [Symmetry code: (iv) $x - 1, y, z$.]

is located on a twofold axis and the two H2 atoms bonded to O6 are crystallographically equivalent (Figs. 1*b* and 2*b*). This is not the case in the *Cc*-type structure, where atom H7 behaves very similarly to what we see in the *C2/c*-type structure, but atom H8 shifts considerably and its hydrogen bond is accepted by a different O atom, O4 (compare Figs. 1*a* and 1*b*). The Cs atom in the *C2/c*-type structure is located on the origin (0, 0, 0), whereas it is slightly offset in the *b* direction in the *Cc*-type structure [$y = -0.009538(17)$] (compare Figs. 1 and 2), which is in concordance with the lower space group symmetry. The ellipsoid drawing of $\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HAsO}_4)$ is given in Fig. 3.

Experimental

The title compound was prepared hydrothermally (Teflon-lined stainless steel bomb, 493 K, nine days, slow furnace cooling) from a mixture of Cs_2CO_3 , Al_2O_3 and $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$, with a volume ratio of approximately 1:1:3. The Teflon containers were then filled with distilled water to about 80% of their inner volume. The pH value of the starting and final solutions was approximately 1 and 0.5, respectively. $\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HAsO}_4)$ formed as colourless prismatic crystals up to 0.8 mm in length (yield *ca* 60%) and was accompanied by hexagonal tabular crystals of $\text{RbFe}(\text{HPO}_4)_2$ -type (Lii & Wu, 1994) $\text{CsAl}(\text{HAsO}_4)_2$ (*ca* 5%) and an uninvestigated amorphous mass (*ca* 35%) (Schwendtner & Kolitsch, 2005c).

Crystal data

$\text{CsAl}(\text{H}_2\text{AsO}_4)_2(\text{HAsO}_4)$	$Z = 4$
$M_r = 581.69$	$D_x = 3.756 \text{ Mg m}^{-3}$
Monoclinic, <i>Cc</i>	Mo $K\alpha$ radiation
$a = 4.634(1) \text{ \AA}$	$\mu = 13.32 \text{ mm}^{-1}$
$b = 14.672(3) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 15.153(3) \text{ \AA}$	Prism, colourless
$\beta = 93.11(3)^\circ$	$0.10 \times 0.09 \times 0.02 \text{ mm}$
$V = 1028.7(4) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	4467 measured reflections
φ and ω scans	4456 independent reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski <i>et al.</i> , 2003)	4221 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.349$, $T_{\max} = 0.777$	$R_{\text{int}} = 0.032$
	$\theta_{\max} = 35.0^\circ$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.024$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$\Delta\rho_{\max} = 0.81 \text{ e \AA}^{-3}$
$wR(F^2) = 0.061$	$\Delta\rho_{\min} = -1.08 \text{ e \AA}^{-3}$
$S = 1.03$	Extinction correction: <i>SHELXL97</i>
4456 reflections	Extinction coefficient: 0.00190 (12)
161 parameters	Absolute structure: Flack (1983), 2187 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.506 (9)
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 4.178P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

The choice of space group *Cc* was based on the following evidence: (i) a refinement in space group *C2/c* and using the model of $\text{CsGa}(\text{H}_{1.5}\text{AsO}_4)_2(\text{H}_2\text{AsO}_4)$ (Schwendtner & Kolitsch, 2005*a*) resulted in $R(F) = 0.15$ and high residual electron densities ($6\text{--}3 \text{ e \AA}^{-3}$); application of various probable twin laws did not lead to any improvement. (ii) All intensity statistics showed a distinct preference for non-centrosymmetry, whereas those of $\text{CsM}^{\text{III}}(\text{H}_{1.5}\text{AsO}_4)_2(\text{H}_2\text{AsO}_4)$ ($M^{\text{III}} = \text{Ga}$ and Cr ; Schwendtner & Kolitsch, 2005*a*) clearly indicated centrosymmetry. (iii) A search for higher symmetry using *PLATON*

Table 1
Selected bond lengths (\AA).

Cs1—O7	3.107 (3)	Al1—O6	1.911 (3)
Cs1—O9	3.137 (3)	Al1—O10 ^{iv}	1.926 (3)
Cs1—O12 ⁱ	3.152 (3)	As1—O1	1.669 (2)
Cs1—O1 ⁱⁱ	3.190 (2)	As1—O2	1.677 (2)
Cs1—O8 ⁱⁱⁱ	3.199 (3)	As1—O3	1.683 (3)
Cs1—O6 ⁱⁱⁱ	3.285 (3)	As1—O4	1.734 (3)
Cs1—O3 ⁱⁱⁱ	3.319 (3)	As2—O5	1.657 (2)
Cs1—O11 ^{iv}	3.355 (3)	As2—O6	1.673 (2)
Cs1—O4 ^v	3.386 (3)	As2—O8	1.716 (3)
Cs1—O5 ^{iv}	3.415 (3)	As2—O7	1.718 (3)
Cs1—O11	3.730 (3)	As3—O9	1.668 (2)
Al1—O2	1.889 (3)	As3—O10	1.674 (2)
Al1—O1 ^{iv}	1.892 (3)	As3—O11	1.702 (3)
Al1—O9	1.899 (3)	As3—O12	1.710 (3)
Al1—O5 ^{iv}	1.905 (3)		

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

Table 2
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O4—H4 \cdots O11 ^{vi}	0.82	2.22	2.978 (4)	154
O7—H7 \cdots O10 ⁱ	0.82	2.04	2.801 (4)	154
O8—H8 \cdots O4 ^{vii}	0.82	2.13	2.791 (4)	137
O11—H11 \cdots O3 ^{viii}	0.82	1.76	2.569 (4)	169
O12—H12 \cdots O3 ^v	0.82	1.84	2.641 (4)	167

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

(Spek, 2003) was unsuccessful. (iv) The correlation parameters calculated from the last refinement step were negligible (the largest correlation was between the *z* and *y* coordinates of atom H2). (v) The structure model and the inferred hydrogen-bonding scheme (different from that of the *C2/c* model) are highly plausible. All O—H bonds were generated using the HFIX 147 command. The crystal was refined as a racemic twin.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3017). Services for accessing these data are described at the back of the journal.

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