research communications

CsGa(HAsO$_4$)$_2$, the first Ga representative of the RbAl(HAsO$_4$)$_2$ structure type

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The crystal structure of hydrothermally synthesized (T = 493 K, 7 d) caesium gallium bis[hydrogen arsenate(V)], CsGa(HAsO$_4$)$_2$, was solved by single-crystal X-ray diffraction. The compound crystallizes in the common RbAl(HAsO$_4$)$_2$ structure type ($R32$) and consists of a basic tetrahedral–octahedral framework topology that houses Cs$^+$ cations in its channels. The AsO$_4$ tetrahedron is disordered over two positions with site occupancy factors of 0.946 (1) and 0.054 (1). Strong hydrogen bonds strengthen the network. The structure was refined as inversion twin.

1. Chemical context

Compounds with mixed tetrahedral–octahedral (T–O) framework structures are characterized by a broad range of different atomic arrangements. These topologies result in several interesting properties such as ion exchange (Masquelier *et al.*, 1996) and ion conductivity (Chouchene *et al.*, 2017), as well as unusual piezoelectric (Ren *et al.*, 2015), magnetic (Ouerfelli *et al.*, 2007) or non-linear optical features (frequency doubling; Sun *et al.*, 2017).

CsGa(HAsO$_4$)$_2$ was obtained during our extensive experimental study of the system M^+–M^{3+}–As^{5+}–O–(H) (M^+ = Li, Na, K, Rb, Cs, Ag, Tl, NH$_4$; M^{3+} = Al, Ga, In, Sc, Fe, Cr, Tl), which resulted in the discovery of an unusually large variety of new structure types (Schwendtner & Kolitsch, 2004, 2005, 2007a,b,c, 2017a, 2018a, 2019; Schwendtner, 2006). One atomic arrangement, the RbFe(HPO$_4$)$_2$ type (Lii & Wu, 1994; rhombohedral, $R\bar{3}c$), and its two relatives, the CsAl$_2$As-(HAsO$_4$)$_6$ type (Schwendtner & Kolitsch, 2018a, rhombohedral, $R\bar{3}c$) and the RbAl(HAsO$_4$)$_2$ type (Schwendtner & Kolitsch, 2018a, rhombohedral, $R32$), were found to exhibit a large crystal–chemical flexibility, which allows the incorporation of a wide variety of M^+ and M^{3+} cations. So far the RbFe(HPO$_4$)$_2$-type is represented by eight arsenate members with the following M^+M^{3+} combinations: TlAl, (NH$_4$)Ga, RbIn, RbGa, RbAl, RbFe, CsIn and CsFe (Schwendtner & Kolitsch, 2017b, 2018a,b,c,e). Six arsenates of the CsAl$_2$As-(HAsO$_4$)$_6$ type are known with the following M^+M^{3+} combinations: RbGa, CsGa, TlGa, RbAl, CsAl and CsFe (Schwendtner & Kolitsch, 2018a,c,d). CsGa(HAsO$_4$)$_2$ represents the third representative of the RbAl(HAsO$_4$)$_2$-type atomic arrangement, of which previously only the two M^+M^{3+} combinations RbAl and CsFe (Schwendtner & Kolitsch, 2018a) were known. The 12-coordinated M^+ cations present in
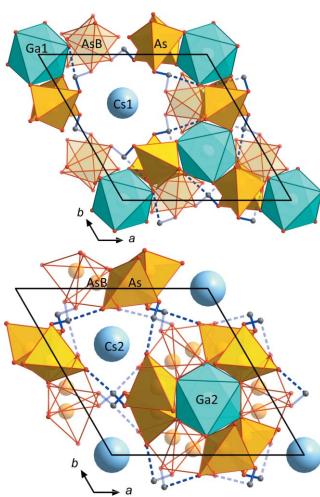
Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H$\cdots$O3^{iii}	0.81 (4)	1.78 (4)	2.589 (5)	175 (6)

Symmetry code: (iii) $-x + y + 1, -x + 1, z$.

these types of compounds are rather large (M = Cs, Rb, Tl and NH$_4$), with ionic radii ranging from 1.70 to 1.88 Å (Shannon, 1976). No members containing K$^+$ or any smaller M^+ cations are presently known, suggesting that the ionic radius of K$^+$ (1.64 Å, Shannon, 1976) is already slightly too small for this type of framework. The ionic radii of the six-coordinated M^{3+} cations (M = Al, Cr, Fe, Ga, In) range from 0.535 to 0.800 Å (Shannon, 1976) and nearly all M^{3+} cations we studied are represented in these types of compounds, with the exception of Sc^{3+} and Tl^{3+}. Syntheses aimed at preparing (NH$_4$)Sc(HAsO$_4$)$_2$, RbSc(HAsO$_4$)$_2$ and TlSc(HAsO$_4$)$_2$ instead led to the crystallization of the diarsenate compounds (NH$_4$)ScAs$_2$O$_7$ (Kolitsch, 2004), RbScAs$_2$O$_7$ (Schwendtner & Kolitsch, 2004) and TlScAs$_2$O$_7$ (Baran *et al.*, 2006), respectively.

There exist only three other Cs–Ga arsenates: The structurally closely related CsGa$_2$As(HAsO$_4$)$_6$ (Schwendtner & Kolitsch, 2018*b*), in which one third of the M^{3+}O$_6$ octahedra are replaced by AsO$_6$ octahedra; CsGa(H$_2$AsO$_4$)(H$_{1.5}$AsO$_4$)$_2$ (Schwendtner & Kolitsch, 2005) which was encountered in the same synthesis batch as the title compound; and Cs$_2$Ga$_3$(As$_3$O$_{10}$)(AsO$_4$)$_2$ (Lin & Lii, 1996).

2. Structural commentary

CsGa(HAsO$_4$)$_2$ is a representative of the RbAl(HAsO$_4$)$_2$ structure type ($R32$; Schwendtner & Kolitsch, 2018*a*) and has a basic tetrahedral–octahedral framework structure featuring interpenetrating channels, which host the M^+ cations (Fig. 1). This structure type is closely related to the RbFe(HPO$_4$)$_2$ structure type ($R\overline{3}c$; Lii & Wu, 1994), the RbAl$_2$As(HAsO$_4$)$_6$ type ($R\overline{3}c$; Schwendtner & Kolitsch, 2018*a*) and the triclinic (NH$_4$)Fe(HPO$_4$)$_2$ type ($P\overline{1}$; Yakubovich, 1993). The fundamental building unit in all these structure types contains M^{3+}O$_6$ octahedra, which are connected *via* their six corners to six protonated AsO$_4$ tetrahedra, thereby forming an
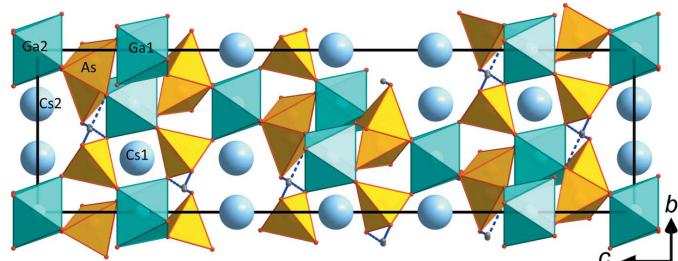

Figure 1
General outline of the crystal structure of CsGa(HAsO$_4$)$_2$ viewed along *a*. Only the main AsO$_4$ tetrahedra are shown (the AsB-centred tetrahedra are omitted for clarity). Hydrogen bonds are shown as blue dotted lines.

Table 2
Selected bond lengths (Å).

Cs1—O4 (6×)	3.338 (3)	As—O1	1.659 (3)
Cs1—O2 (6×)	3.451 (3)	As—O2	1.667 (3)
Cs2—O4 (3×)	3.014 (3)	As—O3	1.691 (3)
Cs2—O1 (3×)	3.445 (3)	As—O4	1.740 (3)
Cs2—O4 (3×)	3.459 (3)	AsB—O1	1.625 (7)
Cs2—O3 (3×)	3.516 (3)	AsB—O3B	1.66 (6)
Ga1—O2 (3×)	1.958 (3)	AsB—O4B^{i}	1.69 (6)
Ga1—O3 (3×)	1.982 (3)	AsB—O2B^{ii}	1.76 (7)
Ga2—O1 (6×)	1.967 (3)		

Symmetry codes: (i) $-y + 1, x - y, z$; (ii) $-x + y, -x, z$.

M^{3+}As$_6$O$_{24}$ unit. These units are in turn connected *via* three corners to other M^{3+}O$_6$ octahedra. The free, protonated corner of each AsO$_4$ tetrahedron forms a medium-to-strong hydrogen bond (Table 1) to the neighbouring M^{3+}As$_6$O$_{24}$ group (Fig. 2*a*,*b*). The M^{3+}As$_6$O$_{24}$ units are arranged in layers perpendicular to the c_{hex} axis (Fig. 1). The units within these

(a)

(b)
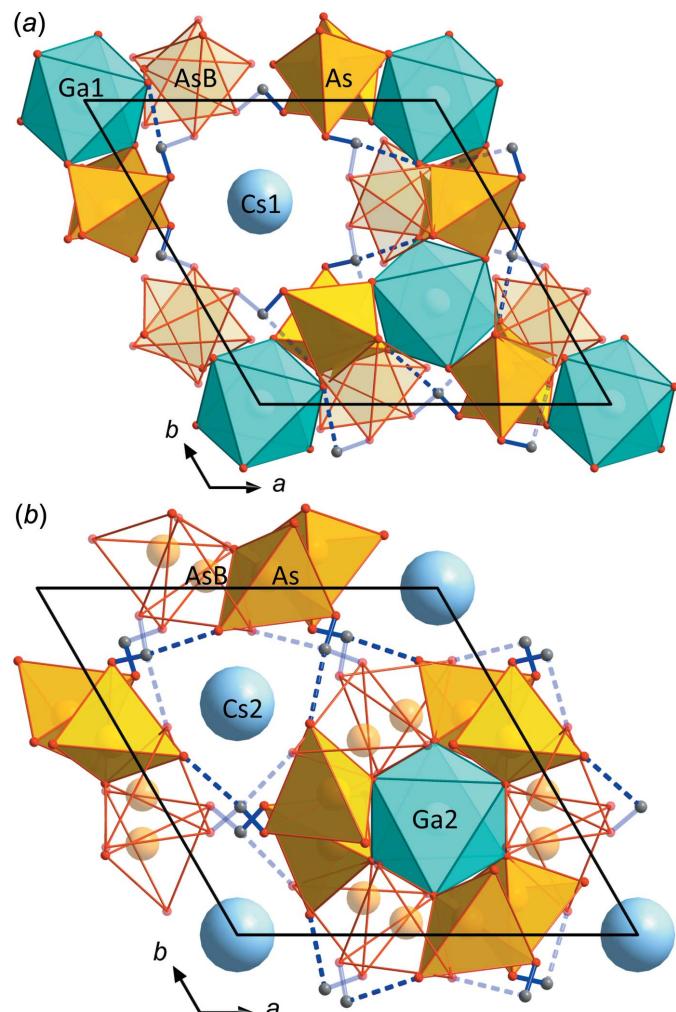
Figure 2
Detailed view of the different layers in the structure of CsGa(HAsO$_4$)$_2$. The alternative AsBO$_4$ tetrahedra, the alternative hydrogen bonds and OB atoms are shown in transparent mode. (*a*) The layer showing the Ga1As$_6$O$_{24}$ group including the alternative AsBO$_4$ tetrahedra. (*b*) The layer showing the Ga2As$_6$O$_{24}$ group including the alternative AsBO$_4$ tetrahedra and the strongly overbonded Cs2 atom in its void.

layers are held together by medium–strong hydrogen bonds (Table 2). Nearly all of the representatives of these closely related structure types show pseudo-hexagonal to pseudo-octahedral crystal habits. In line with this observation, $CsGa(HAsO_4)_2$ forms tiny pseudo-hexagonal platelets.

The two Cs atoms in the framework voids are 12-coordinated. While the average Cs1—O bond length, 3.395 Å, is slightly longer than the grand mean average of 3.377 Å (Gagné & Hawthorne, 2016), it fits the low bond-valence sum (BVS) of 0.84 valence units (v.u.) which was calculated with the bond-valence parameters of Gagné & Hawthorne (2015). In contrast, the average Cs2—O bond length is slightly shorter (3.359 Å) and the individual Cs2—O bond lengths (Table 2) show a much wider bond-length range, resulting in a much too high bond-valence sum of 1.38 v.u. This is mainly caused by four very short Cs2—O bond lengths of only 3.014 Å, although even shorter Cs—O bond lengths, as low as 2.910 Å, have been reported for 12-coordinated Cs^+ cations (Gagné & Hawthorne, 2016).

The Ga atoms at the centre of the two GaO_6 octahedra are also slightly overbonded with BVSs of 3.05 and 3.07 v.u., and average Ga—O bond lengths of 1.970 and 1.967 Å for Ga1 and Ga2, respectively. These values are somewhat shorter than the grand mean average for six-coordinated Ga of 1.978 Å (Gagné & Hawthorne, 2018). The AsO_4 tetrahedra show the typical bond-length geometry of $HAsO_4$ groups with three short and one long As—O bond. The average As—O bond length (1.689 Å) is very close to the observed average of $HAsO_4$ groups (1.687 Å; Schwendtner & Kolitsch, 2019), but the As—O bond length to the protonated O4 atom (1.740 Å, Table 2) is notably longer than the average of 1.728 Å for As—OH bonds in singly protonated AsO_4 groups (Schwendtner & Kolitsch, 2019). The BVS for the As atom is close to ideal with 4.98 v.u. All its O ligands are underbonded to a varying degree, with BVSs ranging from 1.39 v.u. for O4 to 1.92 v.u. for O1.

The As atom is characterized by a split position. The AsB site, 1.27 Å away from the main As position, has a refined occupancy of about 5%. The AsB site shares one apical ligand (O1) with the main AsO_4 tetrahedron and has three additional low-occupancy O atoms (O2B, O3B and O4B) as remaining ligands. The split position can roughly be explained by a mirror plane in (110). The average AsB—O bond length of 1.684 Å is slightly shorter than the corresponding value of the main AsO_4 tetrahedron (1.689 Å), and the AsB—O bonds also show a wider bond-length range (Table 2). The calculated BVS for the AsB site (5.09 v.u.) is reasonable considering the high estimated uncertainty of this value in view of the relatively large positional and bond-length errors for the AsB site (Table 2).

3. Synthesis and crystallization

Small pseudo-hexagonal colorless platelets of $CsGa(HAsO_4)_2$ were prepared hydrothermally (T = 493 K, 7 d) in a Teflon-lined stainless steel autoclave from a mixture of Cs_2CO_3, Ga_2O_3 (approximate molar ratio Cs:Ga of 1:1), arsenic acid and distilled water. Enough arsenic acid was added to keep the

Table 3
Experimental details.

Crystal data	
Chemical formula	$CsGa(HAsO_4)_2$
M_r	482.49
Crystal system, space group	Trigonal, $R32{:}H$
Temperature (K)	293
a, c (Å)	8.481 (1), 27.050 (5)
V (Å^3)	1685.0 (5)
Z	9
Radiation type	Mo $K\alpha$
μ (mm^{-1})	17.24
Crystal size (mm)	$0.03 \times 0.03 \times 0.01$
Data collection	
Diffractometer	Nonius KappaCCD single-crystal four-circle
Absorption correction	Multi-scan (*HKL SCALEPACK*; Otwinowski *et al.*, 2003)
T_{min}, T_{max}	0.626, 0.846
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2738, 1375, 1283
R_{int}	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.757
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.042, 1.07
No. of reflections	1375
No. of parameters	76
No. of restraints	2
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.72, −0.74
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.46 (2)

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

pH between about 1.5 and 0.5. The Teflon cylinders were filled with distilled water up to approximately 80% of their inner volume. Initial and final pH values were about 1.5 and 1, respectively. The platelets were accompanied by large colourless glassy prisms of $CsGa(H_2AsO_4)(H_{1.5}AsO_4)_2$ (Schwendtner & Kolitsch, 2005), which made up about 80% of the reaction products.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

The refinement of $CsGa(HAsO_4)_2$ revealed a considerable residual electron-density peak of 5.1 e Å^{-3} 1.27 Å away from As and 1.62 Å away from the O1 site. The corresponding position can be generated by a mirror plane in (110) and therefore was assumed to be an alternative flipped As position (sharing the same O1 atom), similar to what was encountered in related $TlAl(HAsO_4)$ and $CsIn(HAsO_4)_2$ ($R\bar{3}c$ type; Schwendtner & Kolitsch, 2017b, 2018e). An inclusion of the alternative position led to a considerable drop in the conventional R factor and weight parameters and the highest residual electron densities also decreased considerably. Three electron-density peaks between 1.15 and 1.19 e Å^{-3} close to this AsB position could be attributed to the O ligands of this flipped AsO_4 tetrahedra and, after including them into the

structure model, the conventional R factor dropped from 3.5 to 1.99%. The remaining highest residual electron densities of 0.72 and -0.74 e Å^{-3} are located close to the Cs positions. The occupancy of the alternative As position (Fig. 2) refined to about 5%, while the independently refined occupancy of the main As position was about 95%. For the final refinement, the displacement parameters of the AsB, O2B, O3B and O4B sites were restrained to be the same as that of the main AsO$_4$ tetrahedron position, and the occupancy sums of both tetrahedra were restrained to give a total occupancy of 1.00. The structure was refined as inversion twin with a Flack parameter of 0.46 (2).

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supporting information

CsGa(HAsO₄)₂, the first Ga representative of the RbAl(HAsO₄)₂ structure type

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Computing details

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *HKL 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: *publCIF* (Westrip, 2010).

Caesium gallium bis[hydrogen arsenate(V)]

Crystal data

CsGa(HAsO₄)₂	$D_x = 4.279$ Mg m^{-3}
$M_r = 482.49$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R32:H$	Cell parameters from 1370 reflections
$a = 8.481$ (1) Å	$\theta = 2.3–32.5°$
$c = 27.050$ (5) Å	$\mu = 17.24$ mm^{-1}
$V = 1685.0$ (5) Å^3	$T = 293$ K
$Z = 9$	Tiny hexagonal platelets, colourless
$F(000) = 1962$	$0.03 \times 0.03 \times 0.01$ mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer	1375 independent reflections
	1283 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.018$
φ and ω scans	$\theta_{max} = 32.5°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski *et al.*, 2003)	$h = -12 \rightarrow 12$
	$k = -10 \rightarrow 10$
$T_{min} = 0.626$, $T_{max} = 0.846$	$l = -40 \rightarrow 40$
2738 measured reflections	

Refinement

Refinement on F^2	All H-atom parameters refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 2.6152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.019$	
$wR(F^2) = 0.042$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.72$ e Å^{-3}
1375 reflections	$\Delta\rho_{min} = -0.74$ e Å^{-3}
76 parameters	Extinction correction: SHELXL2016 (Sheldrick, 2015), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]$^{-1/4}$
2 restraints	
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00041 (4)
Secondary atom site location: difference Fourier map	Absolute structure: Refined as an inversion twin
Hydrogen site location: difference Fourier map	Absolute structure parameter: 0.46 (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.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.2225 (4)	0.1039 (5)	0.04039 (9)	0.0161 (5)	
Cs1	0.333333	0.666667	0.166667	0.02717 (16)	
Cs2	0.333333	0.666667	0.00046 (2)	0.02105 (12)	
Ga1	0.000000	0.000000	0.17439 (2)	0.00792 (13)	
Ga2	0.000000	0.000000	0.000000	0.00791 (17)	
As	0.29653 (6)	0.22380 (6)	0.09219 (2)	0.00852 (10)	0.9461 (12)
O2	0.1465 (4)	0.2152 (5)	0.13347 (13)	0.0110 (6)	0.9461 (12)
O3	0.4566 (4)	0.1811 (5)	0.11541 (11)	0.0110 (5)	0.9461 (12)
O4	0.4135 (4)	0.4521 (4)	0.07510 (12)	0.0151 (5)	0.9461 (12)
AsB	0.2984 (10)	0.0710 (10)	0.0923 (3)	0.00852 (10)	0.0540 (12)
O2B	0.081 (9)	0.213 (10)	0.134 (2)	0.0110 (6)	0.0540 (12)
O3B	0.457 (7)	0.265 (8)	0.117 (2)	0.0110 (5)	0.0540 (12)
O4B	0.549 (8)	0.587 (7)	0.077 (2)	0.0151 (5)	0.0540 (12)
H	0.510 (7)	0.474 (8)	0.0874 (17)	0.017 (13)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0123 (12)	0.0253 (16)	0.0101 (11)	0.0090 (14)	−0.0040 (9)	−0.0056 (13)
Cs1	0.0313 (2)	0.0313 (2)	0.0188 (3)	0.01567 (12)	0.000	0.000
Cs2	0.02470 (15)	0.02470 (15)	0.01374 (19)	0.01235 (8)	0.000	0.000
Ga1	0.00859 (18)	0.00859 (18)	0.0066 (3)	0.00430 (9)	0.000	0.000
Ga2	0.0088 (3)	0.0088 (3)	0.0062 (4)	0.00438 (13)	0.000	0.000
As	0.00777 (17)	0.01075 (19)	0.00680 (16)	0.00446 (15)	−0.00031 (14)	0.00020 (14)
O2	0.0107 (14)	0.0127 (13)	0.0097 (12)	0.0060 (13)	0.0045 (11)	0.0008 (10)
O3	0.0110 (13)	0.0138 (14)	0.0104 (12)	0.0078 (10)	−0.0029 (11)	−0.0029 (11)
O4	0.0103 (14)	0.0123 (14)	0.0207 (14)	0.0042 (12)	−0.0013 (12)	0.0052 (12)
AsB	0.00777 (17)	0.01075 (19)	0.00680 (16)	0.00446 (15)	−0.00031 (14)	0.00020 (14)
O2B	0.0107 (14)	0.0127 (13)	0.0097 (12)	0.0060 (13)	0.0045 (11)	0.0008 (10)
O3B	0.0110 (13)	0.0138 (14)	0.0104 (12)	0.0078 (10)	−0.0029 (11)	−0.0029 (11)
O4B	0.0103 (14)	0.0123 (14)	0.0207 (14)	0.0042 (12)	−0.0013 (12)	0.0052 (12)

Geometric parameters (Å, º)

O1—AsB	1.625 (7)	Ga1—O3^{iv}	1.982 (3)
O1—As	1.659 (3)	Ga1—O3^{xi}	1.982 (3)
O1—Ga2	1.967 (3)	Ga1—O3^{xii}	1.982 (3)
O1—Cs2^{i}	3.445 (3)	As—O2	1.667 (3)

Cs1—O4	3.338 (3)	As—O3	1.691 (3)
Cs1—O4^{ii}	3.338 (3)	As—O4	1.740 (3)
Cs1—O4^{iii}	3.338 (3)	As—H	1.99 (6)
Cs1—O4^{iv}	3.338 (3)	O4—H	0.81 (4)
Cs1—O4^{v}	3.338 (3)	AsB—O3B	1.66 (6)
Cs1—O4^{vi}	3.338 (3)	AsB—O4B^{xiii}	1.69 (6)
Cs1—O2^{iv}	3.451 (3)	AsB—O2B^{x}	1.76 (7)
Cs1—O2^{ii}	3.451 (3)	O4B—H	0.88 (7)
Cs1—O2	3.451 (3)	Cs1—O4 (6x)	3.338 (3)
Cs1—O2^{iii}	3.451 (3)	Cs1—O2 (6x)	3.451 (3)
Cs1—O2^{v}	3.451 (3)	Cs2—O4 (3x)	3.014 (3)
Cs1—O2^{vi}	3.451 (3)	Cs2—O1 (3x)	3.445 (3)
Cs1—H	3.46 (5)	Cs2—O4 (3x)	3.459 (3)
Cs2—O4^{iii}	3.014 (3)	Cs2—O3 (3x)	3.516 (3)
Cs2—O4^{ii}	3.014 (3)	Ga1—O2 (3x)	1.958 (3)
Cs2—O4	3.014 (3)	Ga1—O3 (3x)	1.982 (3)
Cs2—O4^{vii}	3.459 (3)	Ga2—O1 (6x)	1.967 (3)
Cs2—O4^{viii}	3.459 (3)	As—O1	1.659 (3)
Cs2—O4^{i}	3.459 (3)	As—O2	1.667 (3)
Cs2—O3^{i}	3.516 (3)	As—O3	1.691 (3)
Cs2—O3^{vii}	3.516 (3)	As—O4	1.740 (3)
Cs2—O3^{viii}	3.516 (3)	AsB—O1	1.625 (7)
Ga1—O2^{ix}	1.958 (3)	AsB—O3B	1.66 (6)
Ga1—O2	1.958 (3)	AsB—O4B^{xiii}	1.69 (6)
Ga1—O2^{x}	1.958 (3)	AsB—O2B^{x}	1.76 (7)
As—O1—Ga2	136.69 (19)	O1^{vii}—Cs2—O4^{i}	124.15 (7)
AsB—O1—Cs2^{i}	87.7 (3)	O1^{i}—Cs2—O4^{i}	46.56 (8)
As—O1—Cs2^{i}	87.31 (11)	O1^{viii}—Cs2—O4^{i}	63.74 (8)
Ga2—O1—Cs2^{i}	127.46 (10)	O4^{vii}—Cs2—O4^{i}	88.64 (8)
O4—Cs1—O4^{ii}	70.99 (9)	O4^{viii}—Cs2—O4^{i}	88.64 (8)
O4—Cs1—O4^{iii}	70.99 (9)	O4^{iii}—Cs2—O3^{i}	159.00 (8)
O4^{ii}—Cs1—O4^{iii}	70.99 (9)	O4^{ii}—Cs2—O3^{i}	115.45 (8)
O4—Cs1—O4^{iv}	99.40 (11)	O4—Cs2—O3^{i}	115.32 (8)
O4^{ii}—Cs1—O4^{iv}	123.13 (11)	O1^{vii}—Cs2—O3^{i}	80.58 (7)
O4^{iii}—Cs1—O4^{iv}	160.35 (10)	O1^{i}—Cs2—O3^{i}	45.29 (7)
O4—Cs1—O4^{v}	123.13 (11)	O1^{viii}—Cs2—O3^{i}	90.53 (7)
O4^{ii}—Cs1—O4^{v}	160.35 (10)	O4^{vii}—Cs2—O3^{i}	43.57 (8)
O4^{iii}—Cs1—O4^{v}	99.40 (11)	O4^{viii}—Cs2—O3^{i}	80.71 (8)
O4^{iv}—Cs1—O4^{v}	70.99 (9)	O4^{i}—Cs2—O3^{i}	46.05 (8)
O4—Cs1—O4^{vi}	160.35 (10)	O4^{iii}—Cs2—O3^{vii}	115.45 (8)
O4^{ii}—Cs1—O4^{vi}	99.40 (11)	O4^{ii}—Cs2—O3^{vii}	115.32 (8)
O4^{iii}—Cs1—O4^{vi}	123.13 (11)	O4—Cs2—O3^{vii}	159.00 (8)
O4^{iv}—Cs1—O4^{vi}	70.99 (9)	O1^{vii}—Cs2—O3^{vii}	45.29 (7)
O4^{v}—Cs1—O4^{vi}	70.99 (9)	O1^{i}—Cs2—O3^{vii}	90.53 (7)
O4—Cs1—O2^{iv}	63.50 (8)	O1^{viii}—Cs2—O3^{vii}	80.58 (7)
O4^{ii}—Cs1—O2^{iv}	126.94 (7)	O4^{vii}—Cs2—O3^{vii}	46.05 (8)
O4^{iii}—Cs1—O2^{iv}	115.11 (8)	O4^{viii}—Cs2—O3^{vii}	43.57 (8)

O4^{iv}—Cs1—O2^{iv}	46.21 (8)	O4^{i}—Cs2—O3^{vii}	80.71 (8)
O4^{v}—Cs1—O2^{iv}	72.50 (8)	O3^{i}—Cs2—O3^{vii}	46.22 (9)
O4^{vi}—Cs1—O2^{iv}	114.43 (8)	O4^{iii}—Cs2—O3^{viii}	115.32 (8)
O4—Cs1—O2^{ii}	114.43 (8)	O4^{ii}—Cs2—O3^{viii}	159.00 (8)
O4^{ii}—Cs1—O2^{ii}	46.21 (8)	O4—Cs2—O3^{viii}	115.45 (8)
O4^{iii}—Cs1—O2^{ii}	72.51 (8)	O1^{vii}—Cs2—O3^{viii}	90.53 (7)
O4^{iv}—Cs1—O2^{ii}	126.94 (8)	O1^{i}—Cs2—O3^{viii}	80.58 (7)
O4^{v}—Cs1—O2^{ii}	115.11 (8)	O1^{viii}—Cs2—O3^{viii}	45.29 (7)
O4^{vi}—Cs1—O2^{ii}	63.50 (8)	O4^{vii}—Cs2—O3^{viii}	80.71 (8)
O2^{iv}—Cs1—O2^{ii}	169.02 (11)	O4^{viii}—Cs2—O3^{viii}	46.05 (8)
O4—Cs1—O2	46.21 (8)	O4^{i}—Cs2—O3^{viii}	43.57 (8)
O4^{ii}—Cs1—O2	72.50 (8)	O3^{i}—Cs2—O3^{viii}	46.22 (9)
O4^{iii}—Cs1—O2	114.43 (8)	O3^{vii}—Cs2—O3^{viii}	46.22 (9)
O4^{iv}—Cs1—O2	63.50 (8)	O2^{ix}—Ga1—O2	91.18 (14)
O4^{v}—Cs1—O2	126.94 (7)	O2^{ix}—Ga1—O2^{x}	91.18 (14)
O4^{vi}—Cs1—O2	115.11 (8)	O2—Ga1—O2^{x}	91.18 (14)
O2^{iv}—Cs1—O2	56.73 (11)	O2^{ix}—Ga1—O3^{iv}	176.98 (13)
O2^{ii}—Cs1—O2	113.48 (5)	O2—Ga1—O3^{iv}	91.84 (14)
O4—Cs1—O2^{iii}	72.50 (8)	O2^{x}—Ga1—O3^{iv}	88.69 (14)
O4^{ii}—Cs1—O2^{iii}	114.43 (8)	O2^{ix}—Ga1—O3^{xi}	88.69 (14)
O4^{iii}—Cs1—O2^{iii}	46.21 (8)	O2—Ga1—O3^{xi}	176.98 (13)
O4^{iv}—Cs1—O2^{iii}	115.11 (8)	O2^{x}—Ga1—O3^{xi}	91.84 (14)
O4^{v}—Cs1—O2^{iii}	63.50 (9)	O3^{iv}—Ga1—O3^{xi}	88.30 (14)
O4^{vi}—Cs1—O2^{iii}	126.94 (8)	O2^{ix}—Ga1—O3^{xii}	91.84 (14)
O2^{iv}—Cs1—O2^{iii}	76.70 (11)	O2—Ga1—O3^{xii}	88.69 (14)
O2^{ii}—Cs1—O2^{iii}	113.48 (5)	O2^{x}—Ga1—O3^{xii}	176.98 (13)
O2—Cs1—O2^{iii}	113.48 (5)	O3^{iv}—Ga1—O3^{xii}	88.30 (14)
O4—Cs1—O2^{v}	126.94 (8)	O3^{xi}—Ga1—O3^{xii}	88.30 (14)
O4^{ii}—Cs1—O2^{v}	115.11 (8)	O2^{ix}—Ga1—Cs2^{xiv}	124.43 (10)
O4^{iii}—Cs1—O2^{v}	63.50 (9)	O2—Ga1—Cs2^{xiv}	124.43 (10)
O4^{iv}—Cs1—O2^{v}	114.43 (8)	O2^{x}—Ga1—Cs2^{xiv}	124.43 (10)
O4^{v}—Cs1—O2^{v}	46.21 (8)	O3^{iv}—Ga1—Cs2^{xiv}	53.54 (10)
O4^{vi}—Cs1—O2^{v}	72.50 (8)	O3^{xi}—Ga1—Cs2^{xiv}	53.54 (10)
O2^{iv}—Cs1—O2^{v}	113.48 (5)	O3^{xii}—Ga1—Cs2^{xiv}	53.54 (10)
O2^{ii}—Cs1—O2^{v}	76.70 (11)	O1—Ga2—O1^{xv}	176.3 (2)
O2—Cs1—O2^{v}	169.02 (11)	O1—Ga2—O1^{ix}	92.14 (11)
O2^{iii}—Cs1—O2^{v}	56.74 (11)	O1^{xv}—Ga2—O1^{ix}	90.55 (19)
O4—Cs1—O2^{vi}	115.11 (8)	O1—Ga2—O1^{xvi}	85.29 (19)
O4^{ii}—Cs1—O2^{vi}	63.50 (8)	O1^{xv}—Ga2—O1^{xvi}	92.13 (11)
O4^{iii}—Cs1—O2^{vi}	126.94 (7)	O1^{ix}—Ga2—O1^{xvi}	176.3 (2)
O4^{iv}—Cs1—O2^{vi}	72.50 (8)	O1—Ga2—O1^{x}	92.14 (11)
O4^{v}—Cs1—O2^{vi}	114.43 (8)	O1^{xv}—Ga2—O1^{x}	85.29 (19)
O4^{vi}—Cs1—O2^{vi}	46.21 (8)	O1^{ix}—Ga2—O1^{x}	92.13 (11)
O2^{iv}—Cs1—O2^{vi}	113.48 (5)	O1^{xvi}—Ga2—O1^{x}	90.55 (19)
O2^{ii}—Cs1—O2^{vi}	56.73 (11)	O1—Ga2—O1^{i}	90.55 (19)
O2—Cs1—O2^{vi}	76.70 (11)	O1^{xv}—Ga2—O1^{i}	92.13 (11)
O2^{iii}—Cs1—O2^{vi}	169.02 (11)	O1^{ix}—Ga2—O1^{i}	85.29 (19)
O2^{v}—Cs1—O2^{vi}	113.48 (5)	O1^{xvi}—Ga2—O1^{i}	92.13 (11)

O4—Cs1—H	13.6 (7)	O1ˣ—Ga2—O1ⁱ	176.3 (2)
O4ⁱⁱ—Cs1—H	84.3 (7)	O1—As—O2	119.51 (15)
O4ⁱⁱⁱ—Cs1—H	71.9 (10)	O1—As—O3	106.29 (15)
O4ⁱᵛ—Cs1—H	94.7 (9)	O2—As—O3	114.75 (17)
O4ᵛ—Cs1—H	109.6 (7)	O1—As—O4	106.75 (16)
O4ᵛⁱ—Cs1—H	164.9 (10)	O2—As—O4	102.97 (16)
O2ⁱᵛ—Cs1—H	53.6 (8)	O3—As—O4	105.36 (17)
O2ⁱⁱ—Cs1—H	126.1 (7)	O1—As—Cs2ⁱ	66.48 (10)
O2—Cs1—H	51.8 (10)	O2—As—Cs2ⁱ	169.73 (12)
O2ⁱⁱⁱ—Cs1—H	62.9 (9)	O3—As—Cs2ⁱ	68.86 (11)
O2ᵛ—Cs1—H	119.3 (10)	O4—As—Cs2ⁱ	66.81 (11)
O2ᵛⁱ—Cs1—H	126.0 (9)	O1—As—Cs1	143.32 (12)
O4ⁱⁱⁱ—Cs2—O4ⁱⁱ	80.04 (10)	O2—As—Cs1	54.72 (12)
O4ⁱⁱⁱ—Cs2—O4	80.04 (10)	O3—As—Cs1	108.02 (11)
O4ⁱⁱ—Cs2—O4	80.04 (10)	O4—As—Cs1	51.41 (11)
O4ⁱⁱⁱ—Cs2—O1ᵛⁱⁱ	90.97 (8)	Cs2ⁱ—As—Cs1	115.260 (12)
O4ⁱⁱ—Cs2—O1ᵛⁱⁱ	74.30 (8)	O1—As—H	117.5 (13)
O4—Cs2—O1ᵛⁱⁱ	153.94 (8)	O2—As—H	110.9 (13)
O4ⁱⁱⁱ—Cs2—O1ⁱ	153.94 (8)	O3—As—H	81.6 (12)
O4ⁱⁱ—Cs2—O1ⁱ	90.97 (8)	O4—As—H	24.0 (12)
O4—Cs2—O1ⁱ	74.30 (8)	Cs2ⁱ—As—H	59.4 (13)
O1ᵛⁱⁱ—Cs2—O1ⁱ	110.22 (4)	Cs1—As—H	56.4 (13)
O4ⁱⁱⁱ—Cs2—O1ᵛⁱⁱⁱ	74.30 (8)	As—O2—Ga1	122.30 (19)
O4ⁱⁱ—Cs2—O1ᵛⁱⁱⁱ	153.94 (8)	As—O2—Cs1	102.06 (14)
O4—Cs2—O1ᵛⁱⁱⁱ	90.97 (8)	Ga1—O2—Cs1	127.77 (14)
O1ᵛⁱⁱ—Cs2—O1ᵛⁱⁱⁱ	110.22 (4)	As—O3—Ga1ˣᵛⁱⁱ	129.62 (19)
O1ⁱ—Cs2—O1ᵛⁱⁱⁱ	110.22 (4)	As—O3—Cs2ⁱ	84.49 (12)
O4ⁱⁱⁱ—Cs2—O4ᵛⁱⁱ	136.20 (4)	Ga1ˣᵛⁱⁱ—O3—Cs2ⁱ	99.51 (12)
O4ⁱⁱ—Cs2—O4ᵛⁱⁱ	78.31 (9)	As—O4—Cs2	132.43 (15)
O4—Cs2—O4ᵛⁱⁱ	131.91 (5)	As—O4—Cs1	104.56 (13)
O1ᵛⁱⁱ—Cs2—O4ᵛⁱⁱ	46.56 (8)	Cs2—O4—Cs1	89.95 (9)
O1ⁱ—Cs2—O4ᵛⁱⁱ	63.74 (8)	As—O4—Cs2ⁱ	85.66 (12)
O1ᵛⁱⁱⁱ—Cs2—O4ᵛⁱⁱ	124.15 (7)	Cs2—O4—Cs2ⁱ	98.06 (9)
O4ⁱⁱⁱ—Cs2—O4ᵛⁱⁱⁱ	78.31 (9)	Cs1—O4—Cs2ⁱ	157.27 (10)
O4ⁱⁱ—Cs2—O4ᵛⁱⁱⁱ	131.91 (5)	As—O4—H	96 (4)
O4—Cs2—O4ᵛⁱⁱⁱ	136.20 (4)	Cs2—O4—H	130 (4)
O1ᵛⁱⁱ—Cs2—O4ᵛⁱⁱⁱ	63.74 (8)	Cs1—O4—H	92 (3)
O1ⁱ—Cs2—O4ᵛⁱⁱⁱ	124.15 (7)	Cs2ⁱ—O4—H	67 (3)
O1ᵛⁱⁱⁱ—Cs2—O4ᵛⁱⁱⁱ	46.56 (8)	O1—AsB—O3B	112 (2)
O4ᵛⁱⁱ—Cs2—O4ᵛⁱⁱⁱ	88.64 (8)	O1—AsB—O4Bˣⁱⁱⁱ	105.6 (18)
O4ⁱⁱⁱ—Cs2—O4ⁱ	131.91 (5)	O3B—AsB—O4Bˣⁱⁱⁱ	104 (3)
O4ⁱⁱ—Cs2—O4ⁱ	136.20 (4)	O1—AsB—O2Bˣ	116 (2)
O4—Cs2—O4ⁱ	78.32 (9)	AsBˣᵛⁱⁱⁱ—O4B—H	105 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H···O3^{xviii}	0.81 (4)	1.78 (4)	2.589 (5)	175 (6)

Symmetry code: (xviii) −*x*+*y*+1, −*x*+1, *z*.