

CsGa(H_{1.5}AsO₄)₂(H₂AsO₄) and isotypic CsCr(H_{1.5}AsO₄)₂(H₂AsO₄): decorated kröhnkite-like chains in two unusual hydrogen arsenates

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Hydrothermally synthesized caesium gallium(III) hydrogen arsenate(V), CsGa(H_{1.5}AsO₄)₂(H₂AsO₄), (I), and isotypic caesium chromium(III) hydrogen arsenate(V), CsCr(H_{1.5}AsO₄)₂(H₂AsO₄), (II), represent a new structure type and stoichiometry among M^I – M^{III} hydrogen arsenates. The crystal structure, determined from single-crystal X-ray diffraction data, is based on an infinite octahedral–tetrahedral chain and can be described as a decorated kröhnkite-like chain. The chains extend parallel to [100] and are separated by ten-coordinated Cs atoms. The hydrogen-bonding scheme comprises one very short symmetry-restricted hydrogen bond, with O···O distances of 2.519 (4) and 2.508 (4) Å in (I) and (II), respectively, and two further medium–strong hydrogen bonds, all of which reinforce the connections between adjacent chains. The average Ga–O and Cr–O bond lengths are 1.973 (15) and 1.980 (13) Å, respectively, and the average As–O bond lengths in the two protonated arsenate groups lie within a very narrow range [1.690 (18)–1.69 (3) Å]. The Cs atom is located on a centre of inversion, while the M^{III} and As2 atoms lie on twofold axes. Relationships to CaBa₂(HPO₄)₂(H₂PO₄)₂ and other compounds containing decorated kröhnkite-type or kröhnkite-like chains are discussed.

Comment

The crystallography and topology of hydrothermally synthesized M^I – M^{III} hydrogen arsenates (M^I = Li, Na, K, Rb, Cs, Tl, Ag, NH₄ and H₃O; M^{III} = Al, Ga, In, Sc, Cr and Fe) are currently being studied in a systematic way by the authors. While our first investigations focused on alkali scandium arsenates (Schwendtner & Kolitsch, 2004a,b; Kolitsch, 2004b), more recent studies have included the remaining M^I and M^{III} cations. So far, these studies have yielded two novel triclinic diarsenate structure types represented by M^I InAs₂O₇ (M = Tl, Rb and NH₄) and AgScAs₂O₇, respectively, and a large number of new representatives for several of the six known

structure types of the compounds with the general formula $A^I M^{III}(HXO_4)_2$ (X = P or As), as well as several new representatives for $M^I M^{III}As_2O_7$ -type diarsenates (Schwendtner & Kolitsch, 2005a,b,c).

The present work reports the novel chain-based crystal structures of two unusual isotypic caesium metal(III) hydrogen arsenates, CsGa(H_{1.5}AsO₄)₂(H₂AsO₄), (I), and CsCr(H_{1.5}AsO₄)₂(H₂AsO₄), (II). The asymmetric unit of the structure type contains one Cs, one M^{III} , two As, six O and three H atoms. The Cs atom is located on a centre of inversion, while the M^{III} and As2 atoms lie on twofold axes. One of the H atoms, involved in a very short hydrogen bond, is split (see discussion below).

The crystal structure contains octahedrally coordinated M^{III} , tetrahedrally coordinated As and ten-coordinated Cs atoms (Figs. 1–3). The average M^{III} –O bond length is 1.973 (15) Å in (I) and 1.980 (13) Å in (II). The latter value is somewhat smaller than the average Cr–O bond distance reported for six-coordinate Cr^{III} (1.999 Å; Baur, 1981).

The two non-equivalent AsO₄ tetrahedra are both protonated. The H atoms involved, *viz.* H1, H2 and H3, all play important roles in the hydrogen-bonding scheme. Atom O4 of the As1O₄ group is bonded to atom H1 on a general position, and the O4–H1 group is involved in a medium–strong hydrogen bond (Tables 2 and 4). In contrast, atom O3 is involved in a very short symmetry-restricted hydrogen bond, with O3···O3' distances of 2.519 (4) and 2.508 (4) Å in (I) and

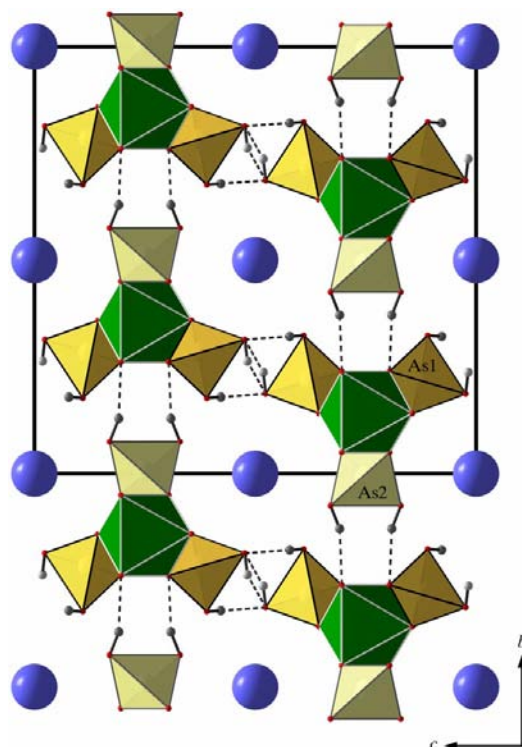


Figure 1
The crystal structure of (I), viewed along [100], in the direction of the infinite decorated kröhnkite-like chains. CdO₆ octahedra are corner-linked to two non-equivalent protonated AsO₄ tetrahedra. The Cs atoms (shown as spheres) separate the chains. Note the very short symmetry-restricted hydrogen bond involving the split H3 atom.

(II), respectively. The split H atom bonded to O3 (H3) could be located experimentally only with difficulty, a situation typical for such strong hydrogen bonds (*e.g.* Clearfield *et al.*, 1976; Giester, 1989; Büchner & Wickleder, 2004). The refinement agrees with observations that the H atom involved in a similarly strong hydrogen bond is invariably located on a half-occupied double-well position slightly off the centre of symmetry (*e.g.* Chevrier *et al.*, 1990, 1993; Macíček *et al.*, 1994; Thomas, 1995; Beran *et al.*, 1997; Olovsson *et al.*, 2001, 2002; Dörsam *et al.*, 2003) and that there is a rapid proton transfer between the two split positions. The two symmetry-equivalent O6 atoms of the doubly protonated As₂O₄ group are each bonded to a H atom (H2) in a general position, and the O6—H2 group is involved in a medium–strong hydrogen bond (Tables 2 and 4), similar to that of the O4—H1 group. The site symmetry of the split H3 atom results in the unusual stoichiometry of the title compounds.

The average As—O bond distances in the two protonated arsenate groups [1.69 (2) and 1.690 (18) Å for As1, and 1.69 (2) and 1.69 (3) Å for As2, in (I) and (II), respectively] are both slightly longer than the mean length in arsenate compounds generally (1.682 Å; Baur, 1981). The slight increase can be attributed to the influence of the protonation and the distinct distortion of the tetrahedra (*cf.* Brown, 1981). As expected, the As—OH bonds are distinctly elongated in comparison with the As—O bonds (Tables 1 and 3), as is typical of protonated AsO₄ tetrahedra (Ferraris, 1970; Ferraris & Ivaldi, 1984). The connectivity of the polyhedral units is rather complex but aesthetic. The $M^{\text{III}}\text{O}_6$ ($M = \text{Ga}$ and Cr) octahedron shares each of its six vertices with protonated AsO₄ tetrahedra. The As1O₄ group acts as a bridge connecting two adjacent $M^{\text{III}}\text{O}_6$ ($M = \text{Ga}$ and Cr) octahedra *via* the O1 and O2 ligands (which are in a *cis* configuration). Thus, an octahedral–tetrahedral kröhnkite-like chain along [100] is formed (see more detailed discussion below). This chain is decorated by the As₂O₄ group, which shares two of its ligands

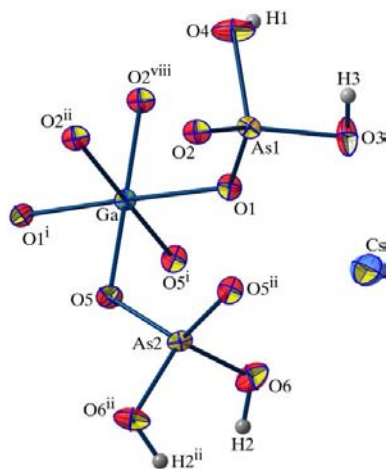


Figure 2

The connectivity in (I), shown with displacement ellipsoids for the non-H atoms at the 70% probability level. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (viii) $x - 1, y, z$.]

(two O5 atoms) with the $M^{\text{III}}\text{O}_6$ ($M = \text{Ga}$ and Cr) octahedron. The very strong hydrogen bond involving atom H3 (see above), as well as the other two, medium–strong, hydrogen bonds, all provide a direct connection between adjacent chains (Fig. 1).

The Cs atom is located on the origin and has ten O ligands within 3.4 Å [the 11th and 12th O-atom neighbours are both at a distance of 3.9094 (19) Å in (I) and 3.921 (2) Å in (II)]. The CsO₁₀ polyhedron closely resembles a flattened pentagonal antiprism, and is characterized by average Cs—O bond lengths of 3.25 (10) and 3.25 (11) Å in (I) and (II), respectively.

Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O'Keeffe (1991). The values obtained are as follows [values for (I) given first]: 1.09/1.11 (Cs), 3.11/3.00 (Ga/Cr), 4.92/4.93 (As1), 4.93/4.93 (As2), 1.97/1.95 (O1), 1.76/1.74 (O2), 1.30/1.30 (O3 is the O ligand involved in very short O3···O3' hydrogen bond donated by the H_{1.5}AsO₄ group), 1.26/1.27 (O4 is the 'normal' OH group of the H_{1.5}AsO₄ group), 1.91/1.89 (O5), 1.30/1.30 (O6 is the OH group of the H₂AsO₄ group) valence units (v.u.). These bond-valence sums are all reasonably close to expected ideal valencies, and confirm that atoms O3, O4 and O6 represent hydroxy groups. The most underbonded O atom (O2) is the acceptor of one of the two medium–strong hydrogen bonds; the acceptor of the remaining hydrogen bond is O3 (Tables 2 and 4).

The infinite octahedral–tetrahedral chain in Cs M^{III} -(H_{1.5}AsO₄)₂(H₂AsO₄) ($M^{\text{III}} = \text{Ga}$ and Cr) may be considered a decorated variant of the widespread kröhnkite-type chain, which is built from MO_6 octahedra corner-linked to bridging XO_4 tetrahedra. This chain is named after kröhnkite, Na₂Cu^{II}(S^{VI}O₄)₂·2H₂O (Dahlman, 1952; Hawthorne & Ferguson, 1975), and is representative of a larger number of compounds containing infinite [$M(\text{XO}_4)_2(\text{H}_2\text{O})_2$] chains, where M is divalent (Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd) or trivalent (Al, Fe, In and Tl), and where X is pentavalent (P and As) or hexavalent (S, Se, Cr, Mo and W) (Fleck *et al.*, 2002; Fleck & Kolitsch, 2003; Kolitsch & Fleck, 2005*a,b*).

While kröhnkite-type chains are not uncommon, decorated versions of either these chains or closely related chains (kröhnkite-like chains according to the classification of Fleck *et al.*, 2002) are rare. Among the few compounds containing such decorated chains is (NH₄)₄Cd(HSe^{IV}O₃)₂(Se^{VI}O₄)₂

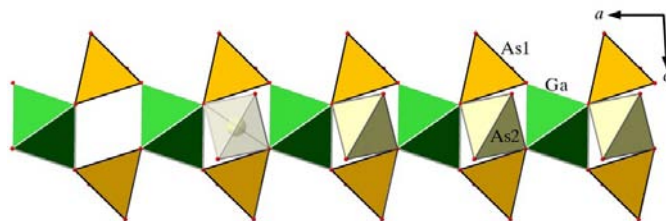


Figure 3

A polyhedral view of the decorated kröhnkite-like chain in (I). The leftmost As₂O₄ tetrahedron has been omitted in order to show the chain more clearly.

(Kolitsch, 2004a), which features a kröhnkite-like infinite chain built of CdO₆ octahedra and pyramidal HSeO₃ groups, and decorated by Se^{VI}O₄ tetrahedra. In Ba₂Ca(HPO₄)₂·(H₂PO₄)₂ (Toumi *et al.*, 1997), CaO₆ octahedra and H₂PO₄ tetrahedra are corner-linked to form kröhnkite-like infinite chains, which are decorated by additional H₂PO₄ tetrahedra. Both Rb₅Er(MoO₄)₄ (Klevtsova & Glinskaya, 1976; note: atomic coordinates are not included in the ICSD) and isotypic Rb₅In(MoO₄)₄ (Tillmanns *et al.*, 2005) contain very similar, but slightly twisted, decorated kröhnkite-like chains based on MO₆ (M = Er and In) octahedra and MoO₄ tetrahedra.

Experimental

Large colourless glassy prisms of (I) were prepared hydrothermally (493 K, 7 d) in a Teflon-lined stainless steel autoclave from a mixture of Cs₂CO₃, Ga₂O₃ (approximate Cs:Ga molar ratio of 1:1), arsenic acid and distilled water. Enough arsenic acid was added to keep the pH between about 1.5 and 0.5. The Teflon cylinders were filled with distilled water up to approximately 80% of their inner volume. The initial and final pH values were about 1.5 and 1, respectively. The prisms were accompanied by a small amount (~20 vol%) of very small hexagonal colourless platelets of CsGa(HAsO₄)₂ (novel structure type, space group R32; Schwendtner & Kolitsch, 2005b,c). Tiny green transparent prisms of (II) were prepared hydrothermally (493 K, 7 d) in a Teflon-lined stainless steel autoclave from a mixture of Cs₂CO₃, Cr₂O₃ (approximate Cs:Cr molar ratio of 1:1), arsenic acid and distilled water. Enough arsenic acid was added to keep the pH between about 1.5 and 0.5. The Teflon cylinders were filled with distilled water up to approximately 80% of their inner volume. The initial and final pH values were 1 and 0.5, respectively. The prisms were accompanied by about 30 vol% of an uninvestigated green material (possibly unreacted Cr₂O₃).

Compound (I)

Crystal data

CsGa(H_{1.5}AsO₄)₂(H₂AsO₄)
 M_r = 624.43
 Monoclinic, C2/c
 a = 4.714 (1) Å
 b = 14.674 (3) Å
 c = 15.162 (3) Å
 β = 93.31 (3)°
 V = 1047.1 (4) Å³
 Z = 4

D_x = 3.961 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 2378 reflections
 θ = 2.0–35.0°
 μ = 15.52 mm⁻¹
 T = 293 (2) K
 Fragment of larger prism, colourless
 0.15 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SCALEPACK; Otwinowski *et al.*, 2003)
 T_{min} = 0.204, T_{max} = 0.653
 4542 measured reflections

2309 independent reflections
 2074 reflections with I > 2σ(I)
 R_{int} = 0.019
 θ_{max} = 35.0°
 h = -7 → 7
 k = -23 → 23
 l = -24 → 24

Refinement

Refinement on F²
 R[F² > 2σ(F²)] = 0.024
 wR(F²) = 0.066
 S = 1.07
 2309 reflections
 92 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F_o²) + (0.039P)² + 2.03P]
 where P = (F_o² + 2F_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.29 e Å⁻³
 Δρ_{min} = -0.98 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00299 (19)

Table 1

Selected interatomic distances (Å) for (I).

As1—O1	1.6714 (15)	Ga—O5 ⁱ	1.9700 (16)
As1—O2	1.6804 (16)	Ga—O2 ⁱⁱ	1.9920 (16)
As1—O3	1.6930 (17)	Cs—O1	3.1496 (16)
As1—O4	1.7179 (19)	Cs—O6	3.156 (2)
As2—O5	1.6693 (15)	Cs—O4 ⁱⁱⁱ	3.213 (2)
As2—O6	1.7115 (18)	Cs—O5 ⁱ	3.3536 (17)
Ga—O1	1.9582 (16)	Cs—O3 ^{iv}	3.373 (2)

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

Table 2

Hydrogen-bond geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O3 ^v	0.87 (4)	1.69 (5)	2.519 (4)	158 (8)
O4—H1...O3 ⁱⁱⁱ	0.82 (4)	1.95 (4)	2.747 (3)	164 (5)
O6—H2...O2 ^{vi}	0.86 (4)	1.98 (4)	2.799 (2)	160 (6)

Symmetry codes: (iii) -x + 1/2, -y + 1/2, -z; (v) -x + 3/2, -y + 1/2, -z; (vi) x - 1/2, y - 1/2, z.

Compound (II)

Crystal data

CsCr(H_{1.5}AsO₄)₂(H₂AsO₄)
 M_r = 606.71
 Monoclinic, C2/c
 a = 4.744 (1) Å
 b = 14.625 (3) Å
 c = 15.127 (3) Å
 β = 93.48 (3)°
 V = 1047.6 (4) Å³
 Z = 4
 D_x = 3.847 Mg m⁻³

Mo Kα radiation
 Cell parameters from 1973 reflections
 θ = 2.0–32.6°
 μ = 13.98 mm⁻¹
 T = 293 (2) K
 Prism, pale green
 0.08 × 0.02 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SCALEPACK; Otwinowski *et al.*, 2003)
 T_{min} = 0.401, T_{max} = 0.767
 3740 measured reflections

1918 independent reflections
 1593 reflections with I > 2σ(I)
 R_{int} = 0.021
 θ_{max} = 32.6°
 h = -7 → 7
 k = -21 → 22
 l = -22 → 22

Refinement

Refinement on F²
 R[F² > 2σ(F²)] = 0.024
 wR(F²) = 0.053
 S = 1.07
 1918 reflections
 89 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F_o²) + (0.023P)² + 2.08P]
 where P = (F_o² + 2F_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.98 e Å⁻³
 Δρ_{min} = -0.80 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00049 (9)

Table 3

Selected interatomic distances (Å) for (II).

As1—O1	1.6727 (18)	Cr—O5 ⁱ	1.9776 (18)
As1—O2	1.6811 (18)	Cr—O2 ⁱⁱ	1.9950 (18)
As1—O3	1.690 (2)	Cs—O1	3.1409 (19)
As1—O4	1.716 (2)	Cs—O6	3.150 (3)
As2—O5	1.6692 (18)	Cs—O4 ⁱⁱⁱ	3.209 (2)
As2—O6	1.713 (2)	Cs—O5 ⁱ	3.354 (2)
Cr—O1	1.9667 (19)	Cs—O3 ^{iv}	3.378 (2)

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

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O3^v$	0.84 (4)	1.68 (4)	2.508 (4)	169 (10)
$O4-H1 \cdots O3^{iii}$	0.82 (4)	1.94 (4)	2.753 (3)	172 (5)
$O6-H2 \cdots O2^{vi}$	0.76 (4)	2.05 (4)	2.786 (3)	161 (5)

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

The split H atom, H3, which is involved in a very short hydrogen bond ($O3 \cdots O3' \simeq 2.5$ Å), could be located experimentally in both (I) and (II) with the help of difference Fourier maps calculated by *PLATON* (Spek, 2003). It was refined with $U_{\text{iso}}(\text{H})$ fixed at 0.04 \AA^2 and the $O3-H3$ bond length restrained to 0.90 (5) Å. The refined site coordinates of atom H3 in (I) and (II) are distinctly off the centre of symmetry at $(\frac{3}{4}, \frac{1}{4}, 0)$, which links atoms $O3$ and $O3'$. The $H3 \cdots H3'$ distance is approximately 0.99 Å in (I) and 0.86 Å in (II). The remaining two H atoms in each arsenate were refined with $O-H$ bond lengths restrained to 0.90 (5) Å. The highest electron-density peak in (I) is 1.05 Å from the As1 site.

For both compounds, data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO* (Otwinowski *et al.*, 2003) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); 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: SQ1217). Services for accessing these data are described at the back of the journal.

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