

New M^+ , M^{3+} -arsenates – the framework structures of $\text{Ag}M^{3+}(\text{HAsO}_4)_2$ ($M^{3+} = \text{Al}, \text{Ga}$) and $M^+\text{GaAs}_2\text{O}_7$ ($M^+ = \text{Na}, \text{Ag}$)

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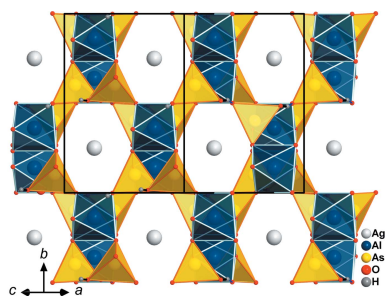
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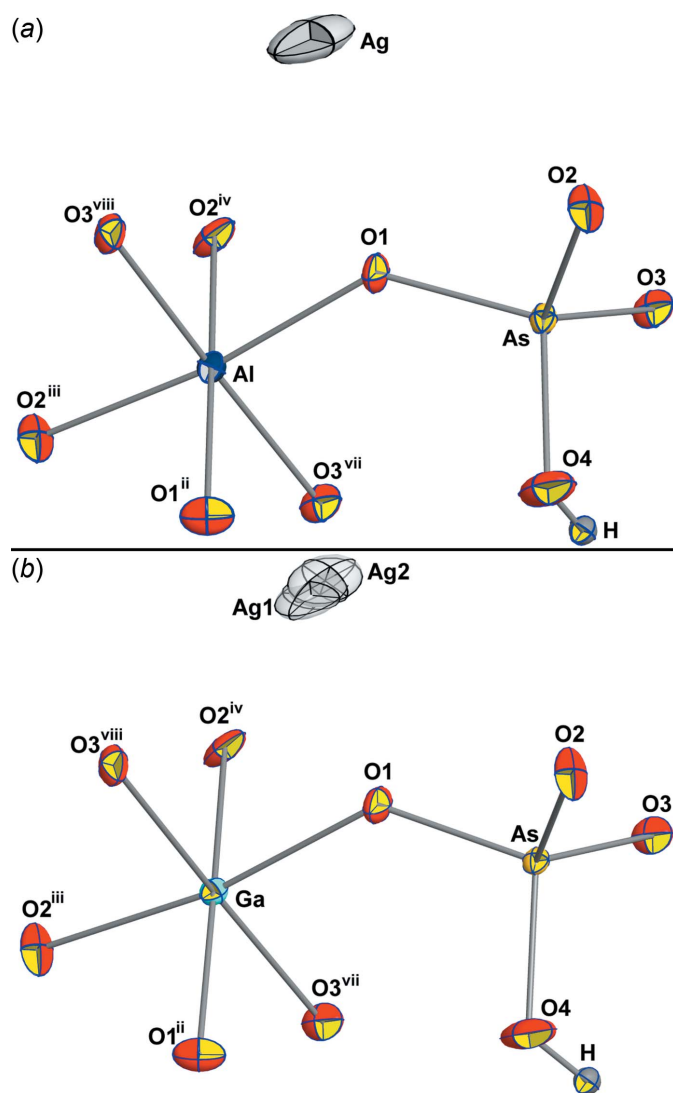
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The crystal structures of hydrothermally synthesized silver(I) aluminium bis[hydrogen arsenate(V)], $\text{AgAl}(\text{HAsO}_4)_2$, silver(I) gallium bis[hydrogen arsenate(V)], $\text{AgGa}(\text{HAsO}_4)_2$, silver gallium diarsenate(V), $\text{AgGaAs}_2\text{O}_7$, and sodium gallium diarsenate(V), $\text{NaGaAs}_2\text{O}_7$, were determined from single-crystal X-ray diffraction data collected at room temperature. The first two compounds are representatives of the MCV-3 structure type known for $\text{KSc}(\text{HAsO}_4)_2$, which is characterized by a three-dimensional anionic framework of corner-sharing alternating $M^{3+}\text{O}_6$ octahedra ($M = \text{Al}, \text{Ga}$) and singly protonated AsO_4 tetrahedra. Intersecting channels parallel to [101] and [110] host the Ag^+ cations, which are positionally disordered in the Ga compound, but not in the Al compound. The hydrogen bonds are relatively strong, with $\text{O} \cdots \text{O}$ donor–acceptor distances of 2.6262 (17) and 2.6240 (19) Å for the Al and Ga compounds, respectively. The two diarsenate compounds are representatives of the $\text{NaAlAs}_2\text{O}_7$ structure type, characterized by an anionic framework topology built of $M^{3+}\text{O}_6$ octahedra ($M = \text{Al}, \text{Ga}$) sharing corners with diarsenate groups, and M^+ cations ($M = \text{Ag}$) hosted in the voids of the framework. Both structures are characterized by a staggered conformation of the As_2O_7 groups.

1. Chemical context

Metal arsenates often form tetrahedral–octahedral framework structures with potentially interesting properties, such as ion conductivity, ion exchange and catalytic properties (Masquelier *et al.*, 1990, 1994*a,b*, 1995, 1996; Medvedev *et al.*, 2003; Ouerfelli *et al.*, 2007*a*, 2008; Pintard-Scrépel *et al.*, 1983; Rousse *et al.*, 2013). A detailed study of the system $M^+M^{3+}\text{As}(\text{O})(\text{H})$ was therefore conducted, and a wide variety of new compounds and structure types were found and have been published (Schwendtner, 2006; Schwendtner & Kolitsch, 2004*a,b*, 2005, 2007*a,b,c,d*). Thus far, three different structure types for $M^+M^{3+}(\text{HAsO}_4)_2$ compounds have been reported. Two of them are very common and were first described for isotopic phosphate compounds. The $(\text{H}_3\text{O})\text{Fe}(\text{HPO}_4)_2$ type (Vencato *et al.*, 1989) is also adopted by $\beta\text{-CsSc}(\text{HAsO}_4)_2$ (Schwendtner & Kolitsch, 2004*b*), while the $(\text{NH}_4)\text{Fe}(\text{HPO}_4)_2$ type (Yakubovich, 1993) is adopted by $\alpha\text{-CsSc}(\text{HAsO}_4)_2$ (Schwendtner & Kolitsch, 2004) and $(\text{NH}_4)\text{Fe}(\text{HAsO}_4)_2$ (Ouerfelli *et al.*, 2014). The $\text{KSc}(\text{HAsO}_4)_2$ type (Schwendtner & Kolitsch, 2004*a*) has so far been the only known example; the two new protonated arsenates presented here are two further representatives of this structure type.




Figure 1

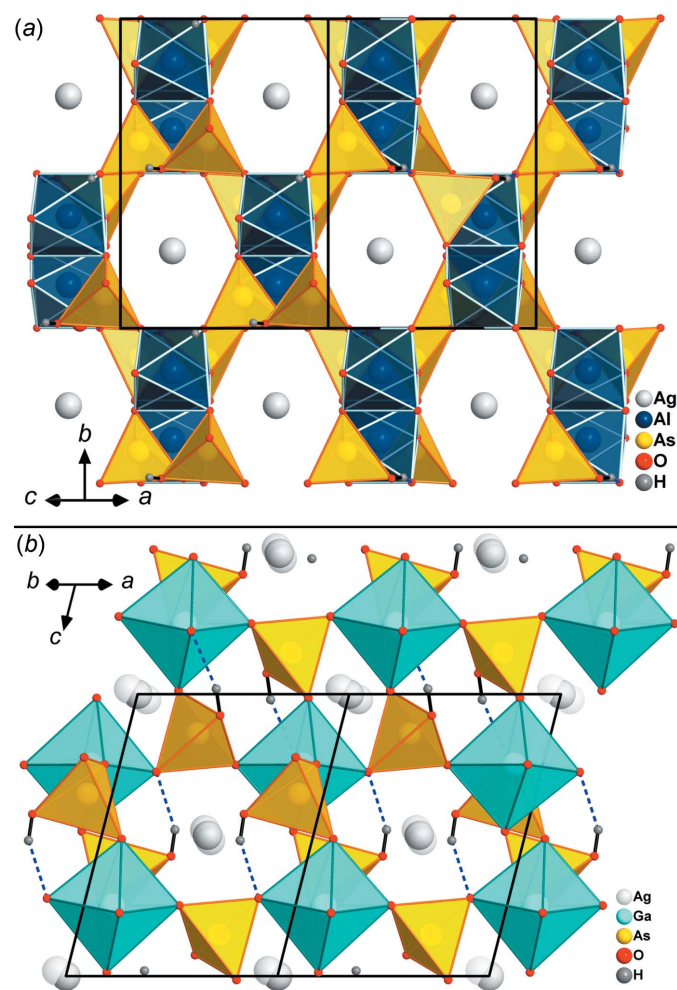
The principal building units of (a) $\text{AgAl}(\text{HAsO}_4)_2$ and (b) $\text{AgGa}(\text{HAsO}_4)_2$, shown as displacement ellipsoids at the 70% probability level. The H atom is shown as a sphere with arbitrary radius. Part (b) shows the split position for Ag in $\text{AgGa}(\text{HAsO}_4)_2$. [Symmetry codes: (ii) $-x, y, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.]

$M^+M^{3+}\text{As}_2\text{O}_7$ compounds crystallize in six known structure types, some of them isotypic to phosphates or silicates. The $\text{CaZrSi}_2\text{O}_7$ type (mineral gittinsite; Roelofsen-Ahl & Peterson, 1989) is also adopted by $\text{LiFeAs}_2\text{O}_7$ (Wang *et al.*, 1994), $\text{LiM}^{3+}\text{As}_2\text{O}_7$ ($M^{3+} = \text{Al, Ga, Sc}$) and $\text{NaScAs}_2\text{O}_7$ (Schwendtner & Kolitsch, 2007*d*). The $\text{NaInAs}_2\text{O}_7$ type (Belam *et al.*, 1997) has no other known members. The $\text{TlInAs}_2\text{O}_7$ type ($M^+ = \text{Tl, Rb, NH}_4$) (Schwendtner, 2006) is also adopted by KFeAs_2O_7 (Ouerfelli *et al.*, 2007*b*). The $\text{RbAlAs}_2\text{O}_7$ type (Boughzala *et al.*, 1993) is also known for $M^{1+} = \text{Tl, Cs}$ (Boughzala & Jouini, 1992), $M^{1+} = \text{K}$ (Boughzala & Jouini, 1995), and is further represented by KGaAs_2O_7 (Lin & Lii, 1996), KCrAs_2O_7 (Siegfried *et al.*, 2004) and the mixed (Al/Fe) compound $\text{TlAl}_{0.78}\text{Fe}_{0.22}\text{As}_2\text{O}_7$ (Ouerfelli *et al.*, 2007*a*). The KAIP_2O_7 type is extremely common for phosphates and also has five examples that are arsenates,

$M^+\text{ScAs}_2\text{O}_7$ with $M^+ = \text{NH}_4$ (Kolitsch, 2004), Rb (Schwendtner & Kolitsch, 2004*a*), and Tl (Baran *et al.*, 2006), as well as $\text{CsCrAs}_2\text{O}_7$ (Bouhassine & Boughzala, 2015), and the mixed (Al/Cr) compound $\text{K}(\text{Al}_{0.75}\text{Cr}_{0.25})\text{As}_2\text{O}_7$ (Bouhassine & Boughzala, 2017). The $\text{NaAlAs}_2\text{O}_7$ type (Driss & Jouini, 1994) is also known for $\text{AgFeAs}_2\text{O}_7$ and $\text{NaFeAs}_2\text{O}_7$ (Ouerfelli *et al.*, 2004), and the $M_1^{2+}M_2^{2+}$ representative $\text{CaCuAs}_2\text{O}_7$ (Chen & Wang, 1996). The two diarsenates presented here also adopt the $\text{NaAlAs}_2\text{O}_7$ structure type.

2. Structural commentary

$\text{AgAl}(\text{HAsO}_4)_2$ and $\text{AgGa}(\text{HAsO}_4)_2$ are isotypic and crystallize in the monoclinic ($C2/c$) microporous framework structure of $\text{KSc}(\text{HAsO}_4)_2$ (Schwendtner & Kolitsch, 2004*a*). The asymmetric unit contains one Ag, one Ga/Al, one As, four O and one H sites (Fig. 1). The Al/Ga atoms lie on a special position (twofold rotation axis) and the Ag^+ cation is situated


Figure 2

View of the framework structure of (a) $\text{AgAl}(\text{HAsO}_4)_2$ along [101] and (b) isotypic $\text{AgGa}(\text{HAsO}_4)_2$ along [110]. The $M^{3+}\text{O}_6$ octahedra ($M = \text{Al, Ga}$) are corner-linked to HAsO_4 tetrahedra. Both views show small micropores in which the Ag^+ cations are situated; the split Ag position (see text) and hydrogen bonds (dashed lines) are indicated in (b).

Table 1
Selected bond lengths (Å) for AgAl(HAsO₄)₂.

Ag1—O1	2.4040 (11)	Al—O3 ^{iv}	1.9167 (10)
Ag1—O3 ⁱ	2.6362 (11)	As—O2	1.6683 (9)
Ag1—O4 ⁱⁱ	2.8202 (13)	As—O1	1.6697 (10)
Ag1—O2	3.1259 (11)	As—O3	1.6710 (11)
Al—O1	1.8920 (10)	As—O4	1.7161 (10)
Al—O2 ⁱⁱⁱ	1.8955 (11)		

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

Table 2
Hydrogen-bond geometry (Å, °) for AgAl(HAsO₄)₂.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O4—H···O2 ^v	0.89 (1)	1.81 (2)	2.6212 (17)	151 (3)

Symmetry code: (v) $x, -y + 1, z + \frac{1}{2}$.

on an inversion centre. In the case of AgGa(HAsO₄)₂, the Ag⁺ cation occupies a split position (Fig. 1*b*), where Ag1 sits on the inversion centre, with a freely refined occupancy of 0.75 (2). The second site (Ag2) is only 0.31 (3) Å away from Ag1 and has a freely refined occupancy of 0.123 (10). In total, this leads to a composition of one Ag atom per formula unit. The slightly distorted M³⁺O₆ octahedra share corners with six hydrogen arsenate tetrahedra to form a three-dimensional, anionic framework structure with narrow irregular channels parallel to [101] and [110] (Fig. 2), which host the Ag⁺ cations. The latter show a rather irregular [6 + 2]-coordination in both compounds. However, it is well known that Ag atoms tolerate a broad spectrum of coordination spheres (Müller-Buschbaum, 2004).

The protonated apex of the AsO₄ tetrahedron is involved in a relatively strong hydrogen bond with O4···O2($x, -y + 1, z + \frac{1}{2}$) = 2.6212 (17) and 2.6240 (19) Å for the Al (Table 2) and Ga compounds (Table 4), respectively, which runs roughly perpendicular to the (101) plane (Fig. 2). The As—OH bond lengths (Tables 1 and 3) are considerably elongated in comparison to the three remaining As—O bonds (Ferraris & Ivaldi, 1984), but at 1.7161 (10) Å for the Al and 1.7096 (12) Å for the Ga compound are slightly shorter than the average As—OH bond length in HAsO₄²⁻ anions of 1.72 (3) Å (Schwendtner, 2008). The bonds to non-protonated O ligands are shorter than the average mean As—O bond length for inorganic arsenates (1.686 Å; Schwendtner, 2008), and fit well with the data for As bonds to non-protonated O atoms in H₁₋₃AsO₄ groups [average 1.669 Å, Schwendtner, 2008; 1.670 Å, AgAl(HAsO₄)₂; 1.675 Å, AgGa(HAsO₄)₂]. The average bond lengths for the AlO₆ and GaO₆ octahedra agree well with published averages (Baur, 1981; Overweg *et al.*, 1999). Bond-valence sums were calculated using the bond-valence parameters of Brown & Altermatt (1985), and amount to 0.88/0.90 (Ag1), 0.89 (Ag2), 3.05/3.16 (Al/Ga), 5.05/5.02 (As), 2.04/2.06 (O1), 1.85/1.85 (O2), 1.90/2.01 (O3) and 1.22/1.21 (O4 = OH; H atom not considered for calculation) valence units for AgAl(HAsO₄)₂ and AgGa(HAsO₄)₂, respectively. These results are reasonably close to the ideal values; the underbonded O2 is an acceptor of the strong

Table 3
Selected bond lengths (Å) for AgGa(HAsO₄)₂.

Ag1—O1	2.3600 (12)	Ag2—O2 ⁱⁱⁱ	3.116 (18)
Ag1—O3 ⁱ	2.5864 (12)	Ag2—O2	3.185 (17)
Ag1—O4 ⁱⁱ	3.0574 (15)	Ga—O1	1.9591 (11)
Ag1—O2	3.1352 (12)	Ga—O2 ^{vi}	1.9641 (11)
Ag2—O1	2.357 (17)	Ga—O3 ^{vii}	1.9799 (12)
Ag2—O1 ⁱⁱⁱ	2.402 (18)	As—O2	1.6719 (11)
Ag2—O3 ⁱ	2.48 (2)	As—O3	1.6753 (12)
Ag2—O3 ^{iv}	2.73 (3)	As—O1	1.6773 (11)
Ag2—O4 ^v	2.83 (2)	As—O4	1.7096 (12)

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

Table 4
Hydrogen-bond geometry (Å, °) for AgGa(HAsO₄)₂.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O4—H···O2 ^{viii}	0.80 (3)	1.89 (3)	2.6240 (19)	153 (3)

Symmetry code: (viii) $x, -y + 1, z + \frac{1}{2}$.

hydrogen bond. Compared to isotypic KSc(HAsO₄)₂, the cell lengths and the hydrogen bonds of the two new compounds are considerably shorter. As a result of the similar ionic radii of Al³⁺ and Ga³⁺, these two compounds have similar unit-cell parameters. The Ga compound is slightly compressed along the *a* axis (smaller β), but elongated along the *b* axis; the *c* axis is not affected.

The two diarsenates AgGaAs₂O₇ and NaGaAs₂O₇ crystallize in space group *P*2₁/*c* and are isotypic to NaAlAs₂O₇ (Driss & Jouini, 1994). The asymmetric unit contains one Ag/Na, one Ga, two As and seven O sites, all of which occupy general positions (Fig. 3). The basic building block is an As₂O₇ group, which is connected to the GaO₆ octahedra by two corners. The other four free O ligands are connected to different GaO₆ octahedra to form a three-dimensional framework structure (Fig. 4). The As2—O_{bridge} distances [1.755 (3), 1.756 (3) Å] are nearly identical to the literature value of 1.755 Å for the average As—O_{bridge} bond length in diarsenates (Schwendtner & Kolitsch, 2007*d*), whereas the As1—O_{bridge} distances [1.781 (3), 1.777 (3) Å] are further elongated. The average bond lengths of both AsO₄ tetrahedra are slightly longer than the literature value of 1.688 Å (Schwendtner & Kolitsch, 2007*d*) for the average As—O bond length in As₂O₇ groups.

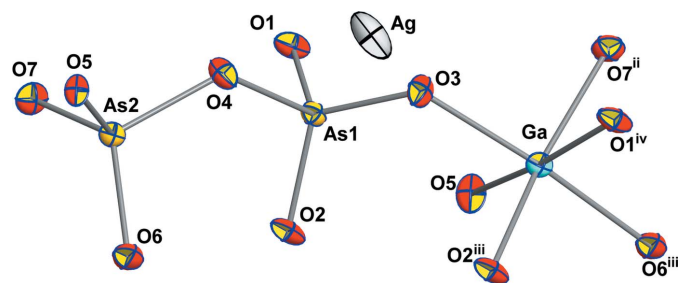


Figure 3
The principal building units of AgGaAs₂O₇ shown as displacement ellipsoids at the 70% probability level. [Symmetry codes: (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $x, -y - \frac{1}{2}, z - \frac{1}{2}$]

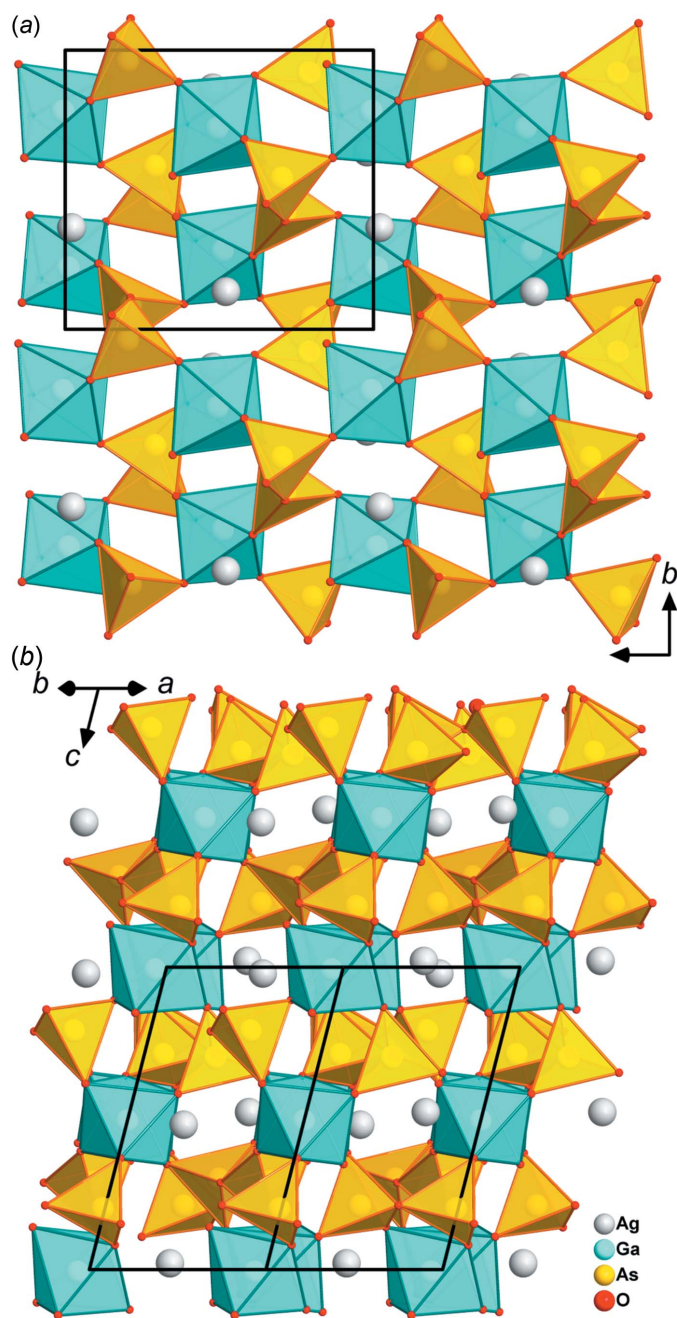


Figure 4
View of the framework structure of $\text{AgGaAs}_2\text{O}_7$ along (a) [100] and (b) [110].

The As—O—As angle is very close to the average value of As_2O_7 groups in a staggered conformation (124.2° , Schwendtner & Kolitsch, 2007*d*) for both compounds (see Tables 5 and 6).

The GaO_6 octahedra are slightly distorted and the average Ga—O bond lengths are close to the literature values ($\sim 1.96 \text{ \AA}$; Overweg *et al.*, 1999). The Na^+ and Ag^+ cations show a strongly distorted octahedral coordination. The calculated bond-valence sums using the parameters of Brown & Altermatt (1985) for Ag, Ga and As, and Wood & Palenik (1999) for Na, amount to 1.06/1.00 (Ag/Na), 3.11/3.11 (Ga),

Table 5
Selected geometric parameters (\AA , $^\circ$) for $\text{AgGa}(\text{As}_2\text{O}_7)$.

Ag—O ⁱ	2.353 (3)	Ga—O ^{6v}	1.985 (3)
Ag—O ⁶ⁱⁱ	2.361 (3)	Ga—O ⁷ⁱ	2.015 (3)
Ag—O ³	2.440 (3)	As1—O ²	1.653 (3)
Ag—O ⁷ⁱⁱⁱ	2.529 (3)	As1—O ¹	1.668 (3)
Ag—O ^{7iv}	2.600 (3)	As1—O ³	1.679 (3)
Ag—O ⁴	2.766 (3)	As1—O ⁴	1.781 (3)
Ga—O ^{2v}	1.939 (3)	As2—O ^{5vi}	1.655 (3)
Ga—O ³	1.957 (3)	As2—O ⁷	1.674 (3)
Ga—O ¹ⁱⁱⁱ	1.973 (3)	As2—O ⁶	1.675 (3)
Ga—O ⁵	1.975 (3)	As2—O ⁴	1.755 (3)
As2—O ⁴ —As1	124.65 (15)		

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

Table 6
Selected geometric parameters (\AA , $^\circ$) for $\text{NaGa}(\text{As}_2\text{O}_7)$.

Na—O ⁱ	2.289 (4)	Ga—O ^{6v}	1.987 (3)
Na—O ⁶ⁱⁱ	2.360 (4)	Ga—O ⁷ⁱ	2.042 (3)
Na—O ³	2.364 (4)	As1—O ²	1.655 (3)
Na—O ⁷ⁱⁱⁱ	2.468 (4)	As1—O ¹	1.664 (3)
Na—O ^{7iv}	2.479 (4)	As1—O ³	1.676 (3)
Na—O ⁴	2.624 (4)	As1—O ⁴	1.777 (3)
Ga—O ^{2v}	1.940 (3)	As2—O ^{5vi}	1.661 (3)
Ga—O ¹ⁱⁱⁱ	1.952 (3)	As2—O ⁶	1.671 (3)
Ga—O ³	1.960 (3)	As2—O ⁷	1.678 (3)
Ga—O ⁵	1.967 (3)	As2—O ⁴	1.756 (3)
As2—O ⁴ —As1	124.73 (19)		

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

4.90/4.93 (As1), 4.96/4.93 (As2), 2.08/2.11 (O1), 1.93/1.92 (O2), 2.01/2.01 (O3), 2.08/2.10 (O4), 1.87/1.86 (O5), 2.03/1.99 (O6), and 2.03/1.99 (O7) valence units for $\text{AgGaAs}_2\text{O}_7$ and $\text{NaGaAs}_2\text{O}_7$, respectively.

3. Synthesis and crystallization

The compounds were grown by hydrothermal synthesis at 493 K (7 d, autogeneous pressure, slow furnace cooling) using Teflon-lined stainless-steel autoclaves with an approximate filling volume of 2 cm^3 . Reagent-grade Ag_2CO_3 , Ga_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, Na_2CO_3 , and $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$ were used as starting reagents in approximate volume ratios of $M^+ : M^{3+} : \text{As}$ of 1:1:2. The vessels were filled with distilled water to about 70% of their inner volumes, which led to final pH values of < 1 for all synthesis batches except $\text{NaGaAs}_2\text{O}_7$ (pH 1.5). The reaction products were washed thoroughly with distilled water, filtered and dried at room temperature.

The two hydrogen arsenates formed pseudo-dipyramidal colourless crystals up to 2 mm in length (yield $> 95\%$ for the Al compound with minor amounts of AgCl , explained by the reaction of Ag^+ with remnants of concentrated hot HCl used for standard cleaning of the Teflon vessels before each new experiment; Fig. 5*a*). The crystals of $\text{AgGa}(\text{HASO}_4)_2$ (Fig. 5*c*) were accompanied by about 20% of $\text{AgGaAs}_2\text{O}_7$ as pseudo-orthorhombic platelets (Fig. 5*d*). $\text{NaGaAs}_2\text{O}_7$ crystallized as small, colourless platelets with a diamond-shaped outline (yield 100%) (Fig. 5*b*).

Table 7
Experimental details.

	AgAl(HAsO ₄) ₂	AgGa(HAsO ₄) ₂	AgGa(AsO ₇)	NaGa(As ₂ O ₇)
Crystal data				
M_r	414.71	457.45	354.55	439.43
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	293	293	293	293
a, b, c (Å)	7.842 (2), 9.937 (2), 8.686 (2)	7.826 (2), 10.216 (2), 8.694 (2)	6.987 (1), 8.266 (2), 9.677 (2)	7.049 (1), 8.368 (2), 9.735 (2)
β (°)	108.45 (3)	107.77 (3)	107.50 (3)	108.47 (3)
V (Å ³)	642.1 (3)	661.9 (3)	533.0 (2)	544.7 (2)
Z	4	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	13.51	16.96	17.55	20.58
Crystal size (mm)	0.15 × 0.08 × 0.07	0.18 × 0.10 × 0.10	0.07 × 0.07 × 0.02	0.10 × 0.08 × 0.02
Data collection				
Diffractometer	Nonius KappaCCD single-crystal four-circle	Nonius KappaCCD single-crystal four-circle	Nonius KappaCCD single-crystal four-circle	Nonius KappaCCD single-crystal four-circle
Absorption correction	Multi-scan (<i>HKL SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)	Multi-scan (<i>HKL SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)	Multi-scan (<i>HKL SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)	Multi-scan (<i>HKL SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)
T_{\min}, T_{\max}	0.236, 0.451	0.150, 0.282	0.373, 0.720	0.233, 0.684
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2751, 1408, 1354	2852, 1460, 1402	3015, 1557, 1336	3849, 1982, 1775
R_{int}	0.011	0.012	0.023	0.022
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.806	0.806	0.704	0.757
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.014, 0.037, 1.10	0.015, 0.037, 1.15	0.033, 0.090, 1.04	0.033, 0.089, 1.05
No. of reflections	1408	1460	1557	1982
No. of parameters	62	73	100	100
No. of restraints	1	0	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	All H-atom parameters refined	–	–
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.55, -0.60	0.66, -0.50	1.54, -1.49	2.29, -2.38

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

Measured X-ray powder diffraction diagrams of the NaGaAs₂O₇ and AgAl(HAsO₄)₂ synthesis batches were

deposited at the International Centre for Diffraction Data under PDF number 57-0162 (Prem *et al.*, 2005) for NaGaAs₂O₇ and 57-0161 (Prem *et al.*, 2005) for AgAl(HAsO₄)₂.

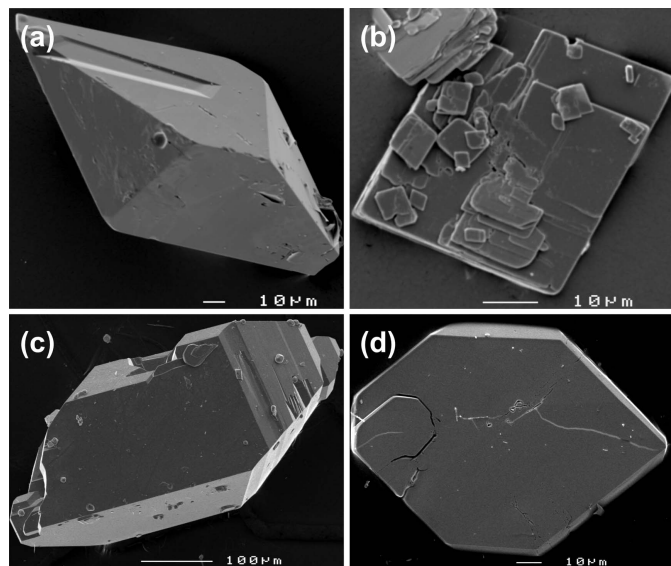


Figure 5
SEM micrographs of hydrothermally synthesized crystals of (a) AgAl(HAsO₄)₂, (b) NaGaAs₂O₇, (c) AgGa(HAsO₄)₂ and (d) AgGaAs₂O₇.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7.

For easier comparison, the atomic positions of the isotopic compounds KSc(HAsO₄)₂ (Schwendtner & Kolitsch, 2004) and NaAlAs₂O₇ (Driss & Jouini, 1994) were used for the final refinement. The O–H distance was restrained to 0.9 (2) Å for AgAl(HAsO₄)₂ and refined freely for AgGa(HAsO₄)₂.

Remaining electron densities are below 1 e Å⁻³ for the two hydrogen arsenates. The remaining maximum and minimum electron densities in the final difference-Fourier maps are located close to the As1 atom (0.87/0.78 Å) for NaGaAs₂O₇, and close to the Ag atom (0.73/0.66 Å) for AgGaAs₂O₇.

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supporting information

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New M^+ , M^{3+} -arsenates – the framework structures of $\text{Ag}M^{3+}(\text{HAsO}_4)_2$ ($M^{3+} = \text{Al}$, Ga) and $M^+\text{GaAs}_2\text{O}_7$ ($M^+ = \text{Na}$, Ag)

Karolina Schwendtner and Uwe Kolitsch

Computing details

For all compounds, 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).

(AgAlHAsO₄)₂ Silver(I) aluminium bis[hydrogen arsenate(V)]

Crystal data

AgAl(HAsO₄)₂
 $M_r = 414.71$
 Monoclinic, *C2/c*
 $a = 7.842$ (2) Å
 $b = 9.937$ (2) Å
 $c = 8.686$ (2) Å
 $\beta = 108.45$ (3)°
 $V = 642.1$ (3) Å³
 $Z = 4$

$F(000) = 768$
 $D_x = 4.290$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1477 reflections
 $\theta = 2.0$ – 35.0 °
 $\mu = 13.51$ mm⁻¹
 $T = 293$ K
 Pseudo-dipyramidal glassy, colourless
 0.15 × 0.08 × 0.07 mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer
 Radiation source: fine-focus sealed tube
 φ and ω scans
 Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski *et al.*, 2003)
 $T_{\min} = 0.236$, $T_{\max} = 0.451$
 2751 measured reflections

1408 independent reflections
 1354 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.011$
 $\theta_{\max} = 34.9$ °, $\theta_{\min} = 3.4$ °
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.014$
 $wR(F^2) = 0.037$
 $S = 1.10$
 1408 reflections
 62 parameters
 1 restraint
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: difference Fourier map
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.890P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.55$ e Å⁻³
 $\Delta\rho_{\min} = -0.60$ e Å⁻³

Extinction correction: SHELXL2016
(Sheldrick, 2015),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0114 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.250000	0.250000	0.000000	0.03518 (7)
Al	0.000000	0.13916 (5)	0.250000	0.00554 (9)
As	0.27443 (2)	0.40001 (2)	0.35945 (2)	0.00508 (5)
O1	0.17964 (13)	0.26607 (10)	0.24940 (12)	0.00972 (16)
O2	0.32668 (13)	0.50141 (10)	0.22800 (11)	0.00973 (16)
O3	0.44856 (12)	0.35479 (10)	0.51919 (11)	0.00870 (15)
O4	0.12010 (13)	0.48544 (12)	0.42496 (12)	0.01492 (19)
H	0.153 (4)	0.487 (3)	0.5324 (12)	0.047 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.06317 (16)	0.02460 (10)	0.03540 (12)	−0.01037 (9)	0.04068 (11)	−0.00702 (8)
Al	0.0059 (2)	0.0053 (2)	0.0052 (2)	0.000	0.00145 (16)	0.000
As	0.00555 (6)	0.00526 (7)	0.00416 (6)	−0.00071 (3)	0.00115 (4)	0.00007 (3)
O1	0.0112 (4)	0.0086 (4)	0.0102 (4)	−0.0057 (3)	0.0045 (3)	−0.0046 (3)
O2	0.0113 (4)	0.0100 (4)	0.0069 (3)	−0.0043 (3)	0.0014 (3)	0.0027 (3)
O3	0.0087 (3)	0.0117 (4)	0.0045 (3)	0.0024 (3)	0.0004 (3)	0.0009 (3)
O4	0.0113 (4)	0.0234 (5)	0.0104 (4)	0.0070 (4)	0.0038 (3)	−0.0026 (4)

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

Ag1—O1 ⁱ	2.4040 (11)	Al—O2 ^{vii}	1.8955 (11)
Ag1—O1	2.4040 (11)	Al—O2 ^v	1.8955 (11)
Ag1—O3 ⁱⁱ	2.6362 (11)	Al—O3 ^{viii}	1.9167 (10)
Ag1—O3 ⁱⁱⁱ	2.6362 (11)	Al—O3 ⁱⁱⁱ	1.9167 (10)
Ag1—O4 ^{iv}	2.8202 (13)	As—O2	1.6683 (9)
Ag1—O4 ^v	2.8202 (13)	As—O1	1.6697 (10)
Ag1—O2	3.1259 (11)	As—O3	1.6710 (11)
Ag1—O2 ⁱ	3.1259 (11)	As—O4	1.7161 (10)
Al—O1	1.8920 (10)	O4—H	0.886 (10)
Al—O1 ^{vi}	1.8920 (10)		
O1—Al—O1 ^{vi}	96.40 (7)	O1 ^{vi} —Al—O3 ⁱⁱⁱ	94.10 (5)
O1—Al—O2 ^{vii}	172.66 (4)	O2 ^{vii} —Al—O3 ⁱⁱⁱ	90.59 (5)

O1 ^{vi} —Al—O2 ^{vii}	88.33 (5)	O2 ^v —Al—O3 ⁱⁱⁱ	92.00 (5)
O1—Al—O2 ^v	88.33 (5)	O3 ^{viii} —Al—O3 ⁱⁱⁱ	176.41 (7)
O1 ^{vi} —Al—O2 ^v	172.66 (4)	O2—As—O1	104.53 (5)
O2 ^{vii} —Al—O2 ^v	87.54 (7)	O2—As—O3	114.68 (5)
O1—Al—O3 ^{viii}	94.10 (5)	O1—As—O3	111.09 (5)
O1 ^{vi} —Al—O3 ^{viii}	83.49 (5)	O2—As—O4	106.25 (6)
O2 ^{vii} —Al—O3 ^{viii}	92.00 (5)	O1—As—O4	110.56 (5)
O2 ^v —Al—O3 ^{viii}	90.59 (5)	O3—As—O4	109.54 (5)
O1—Al—O3 ⁱⁱⁱ	83.49 (5)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H ^{ix} —O2 ^{ix}	0.89 (1)	1.81 (2)	2.6212 (17)	151 (3)

Symmetry code: (ix) $x, -y+1, z+1/2$.

(AgGaHAsO₄2) Silver(I) gallium bis[hydrogen arsenate(V)]

Crystal data

AgGa(HAsO₄)₂
 $M_r = 457.45$
 Monoclinic, $C2/c$
 $a = 7.826$ (2) Å
 $b = 10.216$ (2) Å
 $c = 8.694$ (2) Å
 $\beta = 107.77$ (3)°
 $V = 661.9$ (3) Å³
 $Z = 4$

$F(000) = 840$
 $D_x = 4.590$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1519 reflections
 $\theta = 2.0$ – 35.0 °
 $\mu = 16.96$ mm⁻¹
 $T = 293$ K
 Large pseudo-dipyramidal glassy, colourless
 $0.18 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer
 Radiation source: fine-focus sealed tube
 φ and ω scans
 Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski *et al.*, 2003)
 $T_{\min} = 0.150$, $T_{\max} = 0.282$
 2852 measured reflections

1460 independent reflections
 1402 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 35.0$ °, $\theta_{\min} = 3.4$ °
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -14 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.015$
 $wR(F^2) = 0.037$
 $S = 1.15$
 1460 reflections
 73 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
 $w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 0.940P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.037$
 $\Delta\rho_{\max} = 0.66$ e Å⁻³
 $\Delta\rho_{\min} = -0.50$ e Å⁻³

Extinction correction: SHELXL2016
(Sheldrick, 2015),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0133 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ag1	0.250000	0.250000	0.000000	0.0335 (9)	0.75 (2)
Ag2	0.284 (3)	0.2351 (14)	0.019 (2)	0.0316 (18)	0.123 (10)
Ga	0.000000	0.13670 (2)	0.250000	0.00500 (5)	
As	0.27567 (2)	0.39556 (2)	0.35733 (2)	0.00482 (5)	
O1	0.18942 (15)	0.26190 (10)	0.24943 (13)	0.00983 (18)	
O2	0.32045 (15)	0.49738 (11)	0.22405 (13)	0.01055 (19)	
O3	0.45491 (14)	0.35629 (11)	0.51333 (13)	0.00948 (18)	
O4	0.11608 (16)	0.46896 (14)	0.42534 (15)	0.0169 (2)	
H	0.148 (4)	0.487 (3)	0.519 (4)	0.033 (8)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.051 (2)	0.0368 (14)	0.0271 (9)	−0.0173 (12)	0.0327 (12)	−0.0125 (9)
Ag2	0.049 (4)	0.0249 (16)	0.035 (3)	−0.015 (2)	0.034 (3)	−0.0064 (14)
Ga	0.00555 (9)	0.00478 (9)	0.00482 (9)	0.000	0.00182 (6)	0.000
As	0.00564 (7)	0.00525 (7)	0.00364 (7)	−0.00073 (4)	0.00153 (5)	−0.00003 (4)
O1	0.0114 (4)	0.0093 (4)	0.0101 (5)	−0.0057 (3)	0.0053 (4)	−0.0045 (3)
O2	0.0122 (4)	0.0110 (4)	0.0068 (4)	−0.0060 (3)	0.0003 (3)	0.0036 (4)
O3	0.0085 (4)	0.0135 (4)	0.0053 (4)	0.0032 (3)	0.0004 (3)	0.0011 (4)
O4	0.0116 (5)	0.0299 (6)	0.0094 (5)	0.0081 (4)	0.0035 (4)	−0.0047 (4)

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

Ag1—O1 ⁱ	2.3600 (12)	Ag2—O2	3.185 (17)
Ag1—O1	2.3600 (12)	Ga—O1	1.9591 (11)
Ag1—O3 ⁱⁱ	2.5864 (12)	Ga—O1 ^{vi}	1.9591 (11)
Ag1—O3 ⁱⁱⁱ	2.5864 (12)	Ga—O2 ^{vii}	1.9641 (11)
Ag1—O4 ^{iv}	3.0574 (15)	Ga—O2 ^v	1.9641 (11)
Ag1—O4 ^v	3.0574 (15)	Ga—O3 ^{viii}	1.9799 (12)
Ag1—O2	3.1352 (12)	Ga—O3 ⁱⁱⁱ	1.9799 (12)
Ag2—O1	2.357 (17)	As—O2	1.6719 (11)
Ag2—O1 ⁱ	2.402 (18)	As—O3	1.6753 (12)
Ag2—O3 ⁱⁱ	2.48 (2)	As—O1	1.6773 (11)
Ag2—O3 ⁱⁱⁱ	2.73 (3)	As—O4	1.7096 (12)

Ag2—O4 ^v	2.83 (2)	O4—H	0.80 (3)
Ag2—O2 ⁱ	3.116 (18)		
O1—Ga—O1 ^{vi}	98.48 (7)	O3 ^{viii} —Ga—O3 ⁱⁱⁱ	175.86 (6)
O1—Ga—O2 ^{vii}	171.19 (5)	O2—As—O3	114.16 (6)
O1 ^{vi} —Ga—O2 ^{vii}	87.59 (5)	O2—As—O1	104.63 (6)
O1—Ga—O2 ^v	87.59 (5)	O3—As—O1	110.64 (6)
O1 ^{vi} —Ga—O2 ^v	171.19 (5)	O2—As—O4	107.25 (7)
O2 ^{vii} —Ga—O2 ^v	87.12 (7)	O3—As—O4	110.16 (6)
O1—Ga—O3 ^{viii}	94.82 (5)	O1—As—O4	109.80 (6)
O1 ^{vi} —Ga—O3 ^{viii}	82.46 (5)	O2—As—O3	114.16 (6)
O2 ^{vii} —Ga—O3 ^{viii}	92.29 (5)	O2—As—O1	104.63 (6)
O2 ^v —Ga—O3 ^{viii}	90.71 (5)	O3—As—O1	110.64 (6)
O1—Ga—O3 ⁱⁱⁱ	82.46 (5)	O2—As—O4	107.25 (7)
O1 ^{vi} —Ga—O3 ⁱⁱⁱ	94.82 (5)	O3—As—O4	110.16 (6)
O2 ^{vii} —Ga—O3 ⁱⁱⁱ	90.71 (5)	O1—As—O4	109.80 (6)
O2 ^v —Ga—O3 ⁱⁱⁱ	92.29 (5)		

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

Hydrogen-bond geometry (Å, °)

<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>
O4—H...O2 ^{ix}	0.80 (3)	1.89 (3)	2.6240 (19)	153 (3)

Symmetry code: (ix) $x, -y+1, z+1/2$.

(AgGaAs₂O₇) Silver(I) gallium diarsenate(V)

Crystal data

AgGa(As₂O₇)
 $M_r = 439.43$
 Monoclinic, $P2_1/c$
 $a = 7.049$ (1) Å
 $b = 8.368$ (2) Å
 $c = 9.735$ (2) Å
 $\beta = 108.47$ (3)°
 $V = 544.7$ (2) Å³
 $Z = 4$

$F(000) = 800$
 $D_x = 5.359$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2105 reflections
 $\theta = 2.0$ – 32.6 °
 $\mu = 20.58$ mm⁻¹
 $T = 293$ K
 Pseudo-orthorhombic platelets, colourless
 $0.10 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer
 Radiation source: fine-focus sealed tube
 φ and ω scans
 Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski *et al.*, 2003)
 $T_{\min} = 0.233$, $T_{\max} = 0.684$
 3849 measured reflections

1982 independent reflections
 1775 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 32.5$ °, $\theta_{\min} = 3.1$ °
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.089$
 $S = 1.05$
 1982 reflections
 100 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.6339P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.38 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag	0.81152 (5)	0.13552 (4)	0.47918 (4)	0.02028 (11)
Ga	0.28442 (6)	0.28038 (5)	0.49133 (4)	0.00810 (11)
As1	0.52020 (5)	0.41622 (4)	0.28916 (4)	0.00783 (10)
As2	0.94310 (5)	0.54112 (4)	0.29927 (4)	0.00759 (10)
O1	0.3828 (4)	0.4083 (3)	0.1148 (3)	0.0108 (5)
O2	0.5231 (4)	0.5961 (3)	0.3601 (3)	0.0118 (5)
O3	0.4848 (4)	0.2646 (3)	0.3914 (3)	0.0107 (5)
O4	0.7697 (4)	0.3871 (3)	0.2876 (3)	0.0118 (5)
O5	0.1621 (4)	0.4491 (3)	0.3489 (3)	0.0117 (5)
O6	0.9278 (4)	0.6807 (3)	0.4187 (3)	0.0126 (5)
O7	0.8992 (4)	0.6146 (3)	0.1321 (3)	0.0113 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag	0.01549 (17)	0.01302 (15)	0.0269 (2)	-0.00362 (10)	-0.00097 (13)	0.00458 (11)
Ga	0.0088 (2)	0.00743 (18)	0.00749 (19)	0.00004 (12)	0.00177 (15)	0.00004 (12)
As1	0.00867 (19)	0.00705 (17)	0.00701 (17)	-0.00073 (11)	0.00144 (13)	-0.00004 (11)
As2	0.00788 (18)	0.00726 (17)	0.00707 (18)	0.00035 (11)	0.00158 (13)	0.00016 (11)
O1	0.0143 (13)	0.0076 (11)	0.0076 (11)	0.0007 (9)	-0.0008 (10)	0.0002 (8)
O2	0.0133 (13)	0.0080 (11)	0.0113 (12)	-0.0024 (9)	0.0002 (10)	-0.0026 (9)
O3	0.0125 (12)	0.0096 (11)	0.0114 (11)	0.0030 (9)	0.0056 (10)	0.0040 (9)
O4	0.0104 (12)	0.0080 (11)	0.0164 (13)	-0.0007 (9)	0.0033 (10)	0.0003 (9)
O5	0.0075 (11)	0.0128 (11)	0.0144 (13)	0.0043 (9)	0.0030 (10)	0.0060 (10)
O6	0.0122 (13)	0.0141 (12)	0.0120 (12)	-0.0042 (10)	0.0043 (10)	-0.0052 (10)
O7	0.0129 (13)	0.0124 (12)	0.0074 (11)	0.0015 (9)	0.0013 (10)	0.0020 (9)

Geometric parameters (Å, °)

Ag—O1 ⁱ	2.353 (3)	Ga—O6 ^v	1.985 (3)
Ag—O6 ⁱⁱ	2.361 (3)	Ga—O7 ⁱ	2.015 (3)
Ag—O3	2.440 (3)	As1—O2	1.653 (3)
Ag—O7 ⁱⁱⁱ	2.529 (3)	As1—O1	1.668 (3)
Ag—O7 ^{iv}	2.600 (3)	As1—O3	1.679 (3)
Ag—O4	2.766 (3)	As1—O4	1.781 (3)
Ga—O2 ^v	1.939 (3)	As2—O5 ^{vi}	1.655 (3)
Ga—O3	1.957 (3)	As2—O7	1.674 (3)
Ga—O1 ⁱⁱⁱ	1.973 (3)	As2—O6	1.675 (3)
Ga—O5	1.975 (3)	As2—O4	1.755 (3)
O1 ⁱ —Ag—O6 ⁱⁱ	165.93 (10)	O3—Ga—O7 ⁱ	94.90 (12)
O1 ⁱ —Ag—O3	81.53 (10)	O1 ⁱⁱⁱ —Ga—O7 ⁱ	81.24 (11)
O6 ⁱⁱ —Ag—O3	112.42 (10)	O5—Ga—O7 ⁱ	91.08 (12)
O1 ⁱ —Ag—O7 ⁱⁱⁱ	64.14 (9)	O6 ^v —Ga—O7 ⁱ	86.83 (11)
O6 ⁱⁱ —Ag—O7 ⁱⁱⁱ	106.19 (10)	O2—As1—O1	112.81 (13)
O3—Ag—O7 ⁱⁱⁱ	126.87 (9)	O2—As1—O3	115.14 (14)
O2 ^v —Ga—O3	87.83 (12)	O1—As1—O3	115.19 (13)
O2 ^v —Ga—O1 ⁱⁱⁱ	86.80 (11)	O2—As1—O4	104.27 (13)
O3—Ga—O1 ⁱⁱⁱ	94.54 (11)	O1—As1—O4	104.04 (14)
O2 ^v —Ga—O5	100.89 (12)	O3—As1—O4	103.55 (13)
O3—Ga—O5	85.56 (11)	O5 ^{vi} —As2—O7	108.84 (14)
O1 ⁱⁱⁱ —Ga—O5	172.30 (11)	O5 ^{vi} —As2—O6	112.38 (15)
O2 ^v —Ga—O6 ^v	91.74 (12)	O7—As2—O6	112.71 (14)
O3—Ga—O6 ^v	173.63 (11)	O5 ^{vi} —As2—O4	104.10 (13)
O1 ⁱⁱⁱ —Ga—O6 ^v	91.78 (12)	O7—As2—O4	107.22 (13)
O5—Ga—O6 ^v	88.28 (11)	O6—As2—O4	111.12 (14)
O2 ^v —Ga—O7 ⁱ	167.90 (11)	As2—O4—As1	124.65 (15)

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

(NaGaAs₂O₇) Sodium gallium diarsenate(V)

Crystal data

NaGa(AsO₇) $M_r = 354.55$ Monoclinic, $P2_1/c$ $a = 6.987$ (1) Å $b = 8.266$ (2) Å $c = 9.677$ (2) Å $\beta = 107.50$ (3)° $V = 533.0$ (2) Å³ $Z = 4$ $F(000) = 656$ $D_x = 4.418$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2065 reflections

 $\theta = 3$ – 30° $\mu = 17.55$ mm⁻¹ $T = 293$ KSmall platelets with diamond-shaped outline,
colourless $0.07 \times 0.07 \times 0.02$ mm

Data collection

Nonius KappaCCD single-crystal four-circle diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan

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

$T_{\min} = 0.373$, $T_{\max} = 0.720$

3015 measured reflections

1557 independent reflections

1336 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -9 \rightarrow 9$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.090$

$S = 1.04$

1557 reflections

100 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 1.1P]$

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

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

$\Delta\rho_{\max} = 1.54 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -1.49 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Na	0.8070 (3)	0.1389 (2)	0.4691 (2)	0.0212 (4)
Ga	0.28177 (7)	0.27455 (6)	0.49377 (5)	0.00989 (14)
As1	0.51759 (7)	0.41477 (5)	0.29095 (5)	0.00962 (13)
As2	0.94401 (7)	0.53707 (5)	0.29682 (5)	0.00931 (13)
O1	0.3798 (5)	0.4129 (4)	0.1176 (3)	0.0128 (6)
O2	0.5235 (5)	0.5967 (4)	0.3635 (4)	0.0132 (6)
O3	0.4850 (5)	0.2586 (4)	0.3921 (4)	0.0126 (6)
O4	0.7683 (5)	0.3827 (4)	0.2891 (4)	0.0137 (6)
O5	0.1637 (5)	0.4423 (4)	0.3491 (3)	0.0134 (6)
O6	0.9305 (5)	0.6834 (4)	0.4127 (4)	0.0140 (6)
O7	0.9038 (5)	0.6014 (4)	0.1260 (3)	0.0117 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0190 (10)	0.0122 (9)	0.0286 (10)	-0.0006 (8)	0.0013 (8)	0.0005 (8)
Ga	0.0130 (3)	0.0074 (2)	0.0096 (2)	0.00006 (16)	0.00367 (19)	0.00009 (16)
As1	0.0125 (2)	0.0070 (2)	0.0090 (2)	-0.00080 (15)	0.00274 (17)	0.00001 (15)
As2	0.0120 (2)	0.0073 (2)	0.0086 (2)	0.00045 (15)	0.00308 (17)	0.00032 (15)
O1	0.0175 (17)	0.0087 (14)	0.0102 (14)	-0.0003 (12)	0.0011 (12)	0.0012 (12)
O2	0.0167 (16)	0.0064 (14)	0.0164 (15)	-0.0015 (11)	0.0049 (13)	-0.0028 (12)
O3	0.0166 (16)	0.0087 (14)	0.0146 (15)	0.0022 (12)	0.0080 (13)	0.0035 (12)
O4	0.0098 (15)	0.0121 (14)	0.0198 (16)	0.0002 (12)	0.0055 (12)	0.0001 (12)

O5	0.0130 (16)	0.0124 (14)	0.0142 (15)	0.0039 (12)	0.0029 (13)	0.0043 (12)
O6	0.0188 (17)	0.0120 (15)	0.0139 (14)	-0.0035 (12)	0.0088 (13)	-0.0043 (12)
O7	0.0157 (16)	0.0116 (14)	0.0082 (13)	0.0022 (12)	0.0042 (12)	0.0033 (12)

Geometric parameters (Å, °)

Na—O1 ⁱ	2.289 (4)	Ga—O6 ^v	1.987 (3)
Na—O6 ⁱⁱ	2.360 (4)	Ga—O7 ⁱ	2.042 (3)
Na—O3	2.364 (4)	As1—O2	1.655 (3)
Na—O7 ⁱⁱⁱ	2.468 (4)	As1—O1	1.664 (3)
Na—O7 ^{iv}	2.479 (4)	As1—O3	1.676 (3)
Na—O4	2.624 (4)	As1—O4	1.777 (3)
Ga—O2 ^v	1.940 (3)	As2—O5 ^{vi}	1.661 (3)
Ga—O1 ⁱⁱⁱ	1.952 (3)	As2—O6	1.671 (3)
Ga—O3	1.960 (3)	As2—O7	1.678 (3)
Ga—O5	1.967 (3)	As2—O4	1.756 (3)
O1 ⁱ —Na—O6 ⁱⁱ	163.76 (16)	O1 ⁱⁱⁱ —Ga—O6 ^v	91.80 (14)
O1 ⁱ —Na—O3	80.93 (13)	O3—Ga—O6 ^v	173.31 (13)
O6 ⁱⁱ —Na—O3	114.82 (15)	O5—Ga—O6 ^v	89.46 (14)
O1 ⁱ —Na—O7 ⁱⁱⁱ	65.73 (13)	O2 ^v —Ga—O7 ⁱ	168.13 (13)
O6 ⁱⁱ —Na—O7 ⁱⁱⁱ	99.98 (14)	O1 ⁱⁱⁱ —Ga—O7 ⁱ	80.66 (14)
O3—Na—O7 ⁱⁱⁱ	126.13 (14)	O3—Ga—O7 ⁱ	95.74 (13)
O1 ⁱ —Na—O7 ^{iv}	101.56 (14)	O5—Ga—O7 ⁱ	91.80 (13)
O6 ⁱⁱ —Na—O7 ^{iv}	69.89 (12)	O6 ^v —Ga—O7 ⁱ	87.01 (13)
O3—Na—O7 ^{iv}	137.74 (14)	O2—As1—O1	111.67 (16)
O7 ⁱⁱⁱ —Na—O7 ^{iv}	91.40 (12)	O2—As1—O3	116.27 (16)
O1 ⁱ —Na—O4	116.75 (14)	O1—As1—O3	116.25 (16)
O6 ⁱⁱ —Na—O4	75.75 (13)	O2—As1—O4	103.93 (16)
O3—Na—O4	64.59 (11)	O1—As1—O4	105.16 (17)
O7 ⁱⁱⁱ —Na—O4	168.81 (15)	O3—As1—O4	101.46 (16)
O7 ^{iv} —Na—O4	77.43 (12)	O5 ^{vi} —As2—O6	111.76 (17)
O2 ^v —Ga—O1 ⁱⁱⁱ	87.52 (13)	O5 ^{vi} —As2—O7	108.37 (16)
O2 ^v —Ga—O3	86.31 (14)	O6—As2—O7	113.90 (16)
O1 ⁱⁱⁱ —Ga—O3	94.67 (14)	O5 ^{vi} —As2—O4	103.91 (16)
O2 ^v —Ga—O5	100.04 (14)	O6—As2—O4	112.00 (16)
O1 ⁱⁱⁱ —Ga—O5	172.28 (14)	O7—As2—O4	106.27 (16)
O3—Ga—O5	84.37 (14)	As2—O4—As1	124.73 (19)
O2 ^v —Ga—O6 ^v	92.25 (14)		

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