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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(s–O) = 0.001 Å
R factor = 0.021
wR factor = 0.058
Data-to-parameter ratio = 28.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Guanidinium dihydrogenarsenate

The title compound, $(CH_6N_3)[H_2AsO_4]$, contains a network of guanidinium cations and dihydrogenarsenate anions. The component species interact by way of cation-to-anion N—H···O and anion-to-anion O—H···O hydrogen bonds, the latter leading to infinite sheets of $[H_2AsO_4]^-$ anions.

Comment

The title compound, (I), was prepared as part of ongoing studies of hydrogen-bonding interactions in molecular salts (Wilkinson & Harrison, 2004).
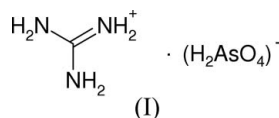
The $[H_2AsO_4]^-$ anion in (I) shows its normal tetrahedral geometry (Fig. 1) about As [mean As—O = 1.684 (2) Å], with the usual distinction between protonated and unprotonated As—O bond lengths (Wilkinson & Harrison, 2004); see Table 1. The three C—N bond lengths in the propeller-shaped $(CH_6N_3)^+$ cation are similar (Table 1), indicating that the usual model of electron delocalization in this species, leading to a C—N bond order of 1.33, is applicable here.

As well as Coulombic forces, the component species in (I) interact by means of a network of cation-to-anion N—H···O and anion-to-anion O—H···O hydrogen bonds, as detailed in Table 2. All the guanidinium atoms participate in hydrogen bonds (one of which, via H8, is bifurcated with notably longer H···O separations than the others), such that the $(CH_6N_3)^+$ cation makes N—H···O links to five adjacent $[H_2AsO_4]^-$ tetrahedra as shown in Fig. 2. For the simple N—H···O bonds, the mean H···O distance = 2.18 Å, mean N···O = 2.951 (3) Å, and the mean N—H···O angle is 150°.
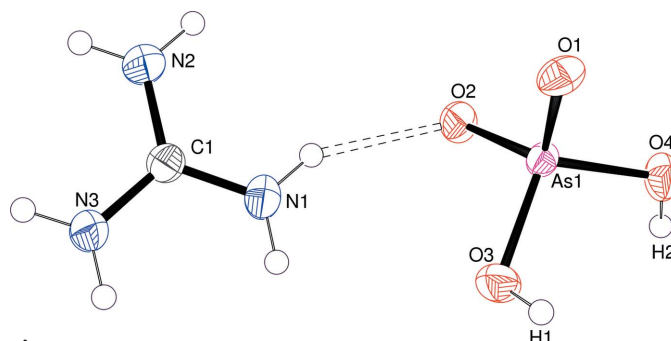
Figure 1
Asymmetric unit of (I) (50% displacement ellipsoids). The hydrogen bond is indicated by a dashed line.
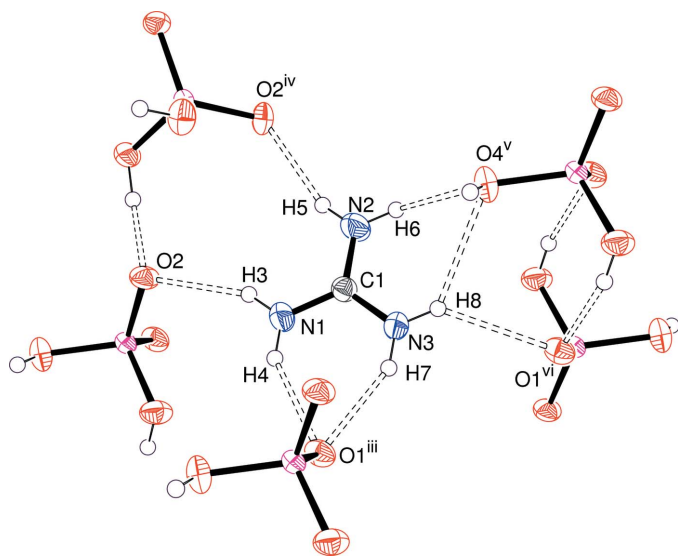
Figure 2
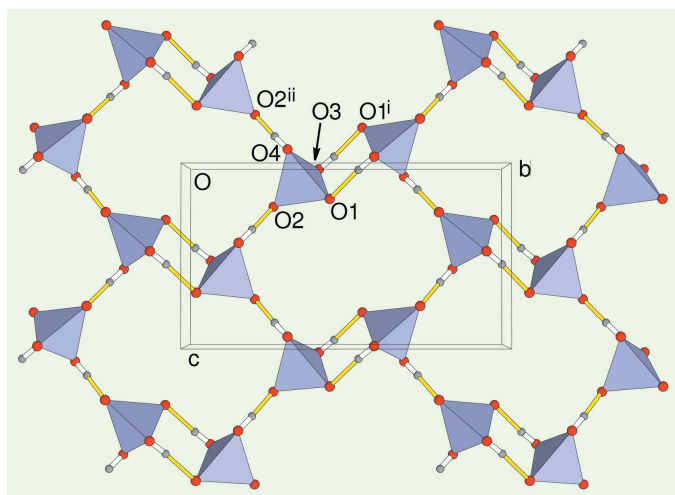Detail of the cation-to-anion N—H···O links (dashed lines) in (I). Symmetry codes are as in Table 2.

Figure 3
Detail of a part of a (100) hydrogen-bonded sheet of $[H_2AsO_4]^-$ groups in (I), in polyhedral representation. Symmetry codes are as in Table 2.

The $[H_2AsO_4]^-$ units are linked into infinite sheets (Fig. 3) by way of the O—H···O hydrogen bonds. The O3—H1···O1^i interaction (see Table 2 for symmetry codes) results in inversion-symmetry-generated dimeric pairs of $[H_2AsO_4]^-$ tetrahedra linked by a double (i.e. O—H···O + O···H—O) hydrogen bond. The O4—H2···O2^{ii} bond links the dimers into an infinite sheet (Fig. 3) propagating in (100). The As···As^i and As···As^{ii} separations are 4.0148 (3) and 5.0190 (3) Å, respectively. If the topological connectivity of the As atoms is considered, a 6^3 sheet (O'Keeffe & Hyde, 1996) arises, i.e. every As node participates in three polyhedral six-ring loops.

The packing for (I) (Fig. 4) results in alternating organic and inorganic layers with respect to the *a* axis direction. The structure of (I) is distinct from other ammonium hydrogenarsenate salts where isolated pairs of tetrahedra (Todd &
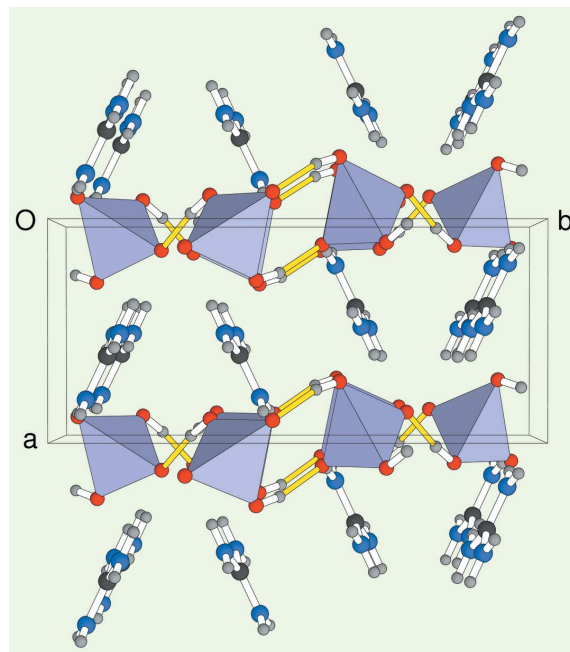

Figure 4
The packing in (I), projected down [001], showing the (100) dihydrogenarsenate layers mediated by guanidinium cations. The N—H···O hydrogen bonds are not shown.

Harrison, 2005) or various kinds of polymeric chains (Wilkinson & Harrison, 2004) occur.

Experimental

An aqueous guanidine solution (0.5 *M*, 10 ml) was added to an H_3AsO_4 solution (0.5 *M*, 10 ml) to give a clear solution. A mass of chunks and blocks of (I) grew as the water evaporated over the course of a few days.

Crystal data

$(CH_6N_3)[H_2AsO_4]$	$D_x = 2.050$ Mg m^{-3}
$M_r = 201.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4819
$a = 6.1571$ (3) Å	reflections
$b = 13.7052$ (6) Å	$\theta = 3.0$–$32.5°$
$c = 7.7208$ (3) Å	$\mu = 5.18$ mm^{-1}
$\beta = 91.715$ (1)°	$T = 295$ (2) K
$V = 651.22$ (5) Å^3	Block, colourless
$Z = 4$	$0.49 \times 0.29 \times 0.13$ mm

Data collection

Bruker SMART1000 CCD	2353 independent reflections
diffractometer	2068 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan	$\theta_{max} = 32.5°$
(*SADABS*; Bruker, 1999)	$h = -9 \rightarrow 9$
$T_{min} = 0.172$, $T_{max} = 0.510$	$k = -18 \rightarrow 20$
7302 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$+ 0.0391P]$
$wR(F^2) = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2353 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*
	Extinction coefficient: 0.0145 (12)

Table 1
Selected bond lengths (Å).

As1—O1	1.6532 (11)	C1—N1	1.314 (2)
As1—O2	1.6538 (10)	C1—N2	1.323 (2)
As1—O4	1.7135 (10)	C1—N3	1.324 (2)
As1—O3	1.7144 (11)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H1$\cdots$O1^{i}	0.85	1.83	2.6684 (16)	167
O4—H2$\cdots$O2^{ii}	0.92	1.65	2.5648 (16)	174
N1—H3$\cdots$O2	0.86	2.13	2.9185 (18)	153
N1—H4$\cdots$O1^{iii}	0.86	2.24	2.993 (2)	147
N2—H5$\cdots$O2^{iv}	0.86	2.15	2.955 (2)	157
N2—H6$\cdots$O4^{v}	0.86	2.28	2.994 (2)	140
N3—H7$\cdots$O1^{iii}	0.86	2.11	2.8962 (17)	152
N3—H8$\cdots$O1^{vi}	0.86	2.47	3.1582 (18)	138
N3—H8$\cdots$O4^{v}	0.86	2.55	3.1965 (18)	133

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

The O-bound H atoms were found in difference maps and allowed for as riding in their as-found relative positions with $U_{iso}(H) = 1.2U_{eq}(O)$. The N-bound H atoms were included in the riding model approximation, with N—H = 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) & *ATOMS* (Shape Software, 2004); software used to prepare material for publication: *SHELXL97*.

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