Piperazinium hydrogenarsenate monohydrate

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.019
wR factor = 0.049
Data-to-parameter ratio = 17.6

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

In the title compound, $C_4H_{12}N_2^{2+} \cdot HAsO_4^{2-} \cdot H_2O$, the component species interact by way of N—H···O and O—H···O hydrogen bonds, the latter leading to infinite sheets of $HAsO_4^{2-}$ anions and water molecules containing $R_6^6(18)$ loops. The asymmetric unit contains one anion, one water molecule and half each of two centrosymmetric cations.

Comment

The As^V-containing title compound, (I), (Fig. 1), arose unexpectedly as a result of atmospheric oxidation from a solution-mediated reaction containing As^{III} (Lee & Harrison, 2004). It complements $C_4H_{12}N_2 \cdot 2H_2AsO_4$, (II) (Wilkinson & Harrison, 2007), which contains the same organic cation accompanied by monovalent dihydrogenarsenate anions. Compound (I) is isostructural with its hydrogenphosphate analogue (Riou *et al.*, 1993).

$$H_2N^+ \diagdown \diagup NH_2^+ \quad \cdot \quad (HAsO_4)^{2-} \quad \cdot \quad H_2O$$

$$(I)$$
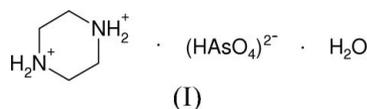
The tetrahedral $HAsO_4^{2-}$ anion in (I) shows three short As—O links with formal partial double-bond character, and one longer As—OH bond (Table 1). The mean As—O bond lengths in (I) [1.683 (2) Å] and (II) [1.684 (2) Å] are indistinguishable.
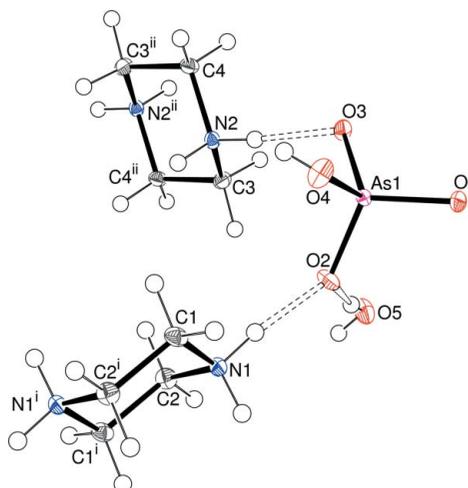

Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are showwn as spheres of arbitrary radius. Hydrogen bonds are indicated by double-dashed lines. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$.]
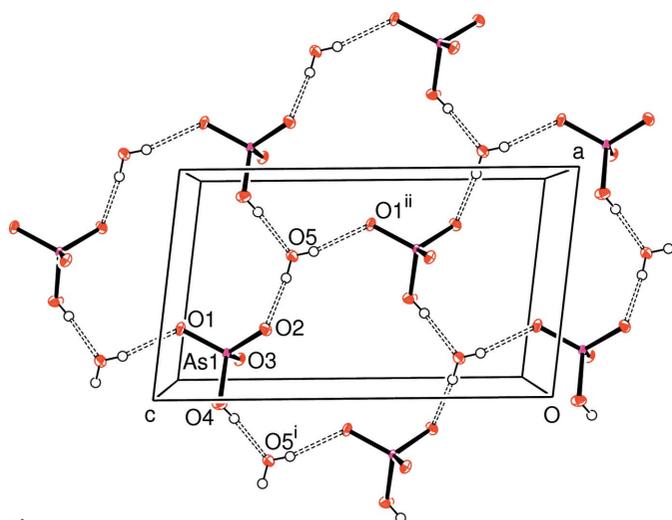
Figure 2
Detail of a part of an (010) hydrogen-bonded sheet of HAsO$_4^{2-}$ groups and water molecules in (I), with H bonds indicated by double-dashed lines. (Symmetry codes as in Table 1.)
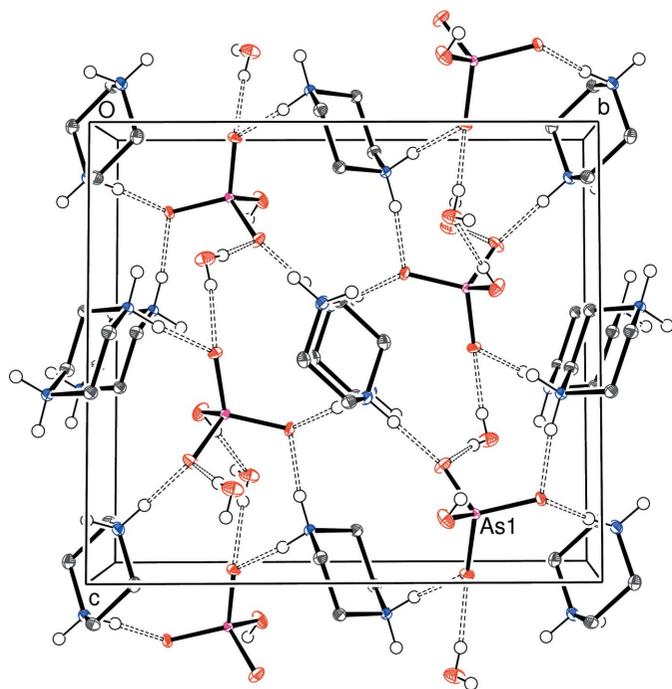

Figure 3
A view down [100] of the unit-cell packing in (I), showing the (010) hydrogenarsenate–water layers mediated by the organic cations. Hydrogen bonds are indicated by double-dashed lines and C-bound H atoms have been omitted for clarity.

The asymmetric unit contains one anion, one water molecule and half each of two centrosymmetric cations. Each cation adopts a typical chair conformation.

As well as Coulombic forces, the component species in (I) interact by way of a network of O—H$\cdots$O and N—H$\cdots$O hydrogen bonds (Table 2). The HAsO$_4^{2-}$ dianions and water molecules are linked into infinite sheets (Fig. 2) propagating in (010) by way of the O—H$\cdots$O bonds. The water molecule accepts one hydrogen bond and makes two hydrogen bonds. Unlike the case in many related molecular salts (Lee &

Harrison, 2003), there are no direct hydrogen-bond links between hydrogenarsenate groups. A supramolecular $R_6^6(18)$ loop (Bernstein *et al.*, 1995) arises from this hydrogen-bond topology.

The hydrogenarsenate–water sheets are bridged by the piperazinium cations, which participate in two strong N—H$\cdots$O interactions from each of their NH$_2$ groups to O atoms of nearby hydrogenarsenate tetrahedra. Thus, there are no hydrogen-bond links between organic cations and water molecules in (I). Overall, a layered architecture (Fig. 3) results, in which layers of organic and inorganic species alternate along [010]. Compound (II) also possesses alternating inorganic and organic layers; in this compound, supramolecular $R_6^6(24)$ loops arise for each circuit of six H$_2$AsO$_4^-$ tetrahedra within a sheet.

Experimental

In an attempt to synthesize an analogue of (H$_3$NCH$_2$CH$_2$NH$_3$)-[AsO$_2$]$_2$ (Lee & Harrison, 2004), aqueous solutions of piperazine (0.1 *M*) and As$^{III}_2$O$_3$ (0.1 *M*) were mixed, resulting in a colourless mixture. Translucent faceted truncated cubes of As$_2$O$_3$ recrystallized after one day. After several months, colourless slabs of (I) were dredged from the viscous liquor.

Crystal data

C$_4$H$_{12}$N$_2^{2+}$·HAsO$_4^{2-}$·H$_2$O	$V = 913.80\,(4)$ Å^3
$M_r = 246.10$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.5093\,(2)$ Å	$\mu = 3.71$ mm^{-1}
$b = 12.5329\,(3)$ Å	$T = 120\,(2)$ K
$c = 11.2873\,(3)$ Å	$0.40 \times 0.28 \times 0.14$ mm
$\beta = 97.0816\,(16)°$	

Data collection

Nonius KappaCCD area-detector diffractometer	15415 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	2094 independent reflections
$T_{min} = 0.318$, $T_{max} = 0.625$	1898 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.049$	
$S = 1.09$	$\Delta\rho_{max} = 0.46$ e Å^{-3}
2094 reflections	$\Delta\rho_{min} = -0.47$ e Å^{-3}
119 parameters	

Table 1
Selected bond lengths (Å).

As1—O1	1.6627 (12)	As1—O3	1.6760 (11)
As1—O2	1.6680 (12)	As1—O4	1.7264 (12)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O5^i	0.842 (10)	1.812 (10)	2.6492 (19)	173 (2)
N1—H1$C\cdots$O2	0.92	1.73	2.6482 (18)	171
N1—H1$D\cdots$O3^{ii}	0.92	1.76	2.6722 (18)	173
N2—H2$C\cdots$O1^{iii}	0.92	1.77	2.6788 (18)	169

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N2—H2D···O3	0.92	1.74	2.6548 (18)	172
O5—H2···O2	0.842 (10)	1.863 (10)	2.6998 (18)	173 (2)
O5—H3···O1^{iv}	0.836 (10)	1.892 (12)	2.7065 (18)	164 (2)

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

O-bound H atoms were found in difference maps and their positions were refined with the restraint O—H = 0.85 (1) Å. C- and N-bonded H atoms were positioned geometrically, with C—H = 0.99 Å and N—H = 0.92 Å, and refined as riding atoms. $U_{iso}(\text{H})$ = $1.2U_{eq}$(carrier) for all H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

Piperazinium hydrogenarsenate monohydrate

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Piperazinium hydrogenarsenate monohydrate

Crystal data

$C_4H_{12}N_2{}^{2+}{\cdot}HAsO_4{}^{2-}{\cdot}H_2O$	$F(000) = 504$
$M_r = 246.10$	$D_x = 1.789$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2149 reflections
$a = 6.5093$ (2) Å	$\theta = 2.9$–27.5°
$b = 12.5329$ (3) Å	$\mu = 3.71$ mm^{-1}
$c = 11.2873$ (3) Å	$T = 120$ K
$\beta = 97.0816$ (16)°	Slab, colourless
$V = 913.80$ (4) Å^3	$0.40 \times 0.28 \times 0.14$ mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	15415 measured reflections
Radiation source: fine-focus sealed tube	2094 independent reflections
Graphite monochromator	1898 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.029$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
$T_{min} = 0.318$, $T_{max} = 0.625$	$h = -8{\rightarrow}8$
	$k = -16{\rightarrow}16$
	$l = -14{\rightarrow}14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.019$	$w = 1/[\sigma^2(F_o{}^2) + (0.0187P)^2 + 0.7794P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.049$	
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2094 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
119 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
3 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0104 (7)
Secondary atom site location: difference Fourier map	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{iso}*/U_{eq}$
As1	0.14908 (2)	0.754902 (12)	0.858124 (14)	0.00805 (8)
O1	0.2714 (2)	0.73938 (9)	0.99528 (11)	0.0136 (3)
O2	0.26775 (19)	0.69220 (10)	0.75530 (11)	0.0159 (3)
O3	0.10970 (18)	0.88403 (9)	0.82395 (10)	0.0124 (2)
O4	−0.09090 (19)	0.69654 (10)	0.85928 (12)	0.0179 (3)
H1	−0.175 (3)	0.7282 (16)	0.8085 (17)	0.021*
C1	−0.0938 (3)	0.51032 (14)	0.60902 (14)	0.0139 (4)
H1A	−0.1834	0.5738	0.5930	0.017*
H1B	−0.1097	0.4841	0.6901	0.017*
C2	0.1611 (3)	0.57581 (13)	0.48176 (15)	0.0141 (3)
H2A	0.3098	0.5916	0.4806	0.017*
H2B	0.0818	0.6419	0.4607	0.017*
N1	0.1258 (2)	0.54061 (11)	0.60339 (13)	0.0133 (3)
H1C	0.1617	0.5949	0.6568	0.016*
H1D	0.2096	0.4831	0.6255	0.016*
N2	0.0015 (2)	0.92247 (11)	0.59340 (12)	0.0105 (3)
H2C	−0.0643	0.8658	0.5532	0.013*
H2D	0.0352	0.9027	0.6719	0.013*
C3	0.1939 (3)	0.94754 (13)	0.54065 (15)	0.0124 (3)
H3A	0.2824	0.8832	0.5426	0.015*
H3B	0.2720	1.0040	0.5883	0.015*
C4	−0.1414 (3)	1.01496 (13)	0.58730 (15)	0.0119 (3)
H4A	−0.0759	1.0740	0.6366	0.014*
H4B	−0.2701	0.9944	0.6200	0.014*
O5	0.6199 (2)	0.78709 (11)	0.70613 (12)	0.0190 (3)
H2	0.509 (2)	0.7551 (15)	0.715 (2)	0.023*
H3	0.645 (4)	0.7727 (17)	0.6371 (11)	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.00945 (11)	0.00745 (10)	0.00729 (12)	−0.00101 (6)	0.00113 (7)	0.00033 (5)
O1	0.0173 (6)	0.0141 (6)	0.0086 (6)	0.0030 (5)	−0.0012 (5)	0.0016 (4)
O2	0.0163 (6)	0.0169 (6)	0.0152 (6)	−0.0024 (5)	0.0046 (5)	−0.0073 (5)
O3	0.0169 (6)	0.0074 (5)	0.0120 (6)	−0.0004 (4)	−0.0019 (5)	0.0021 (4)
O4	0.0135 (6)	0.0175 (6)	0.0225 (7)	−0.0050 (5)	0.0016 (5)	0.0069 (5)

C1	0.0163 (9)	0.0145 (8)	0.0118 (9)	0.0017 (6)	0.0057 (7)	−0.0008 (6)
C2	0.0147 (8)	0.0116 (8)	0.0161 (9)	−0.0020 (6)	0.0025 (7)	0.0008 (6)
N1	0.0163 (7)	0.0109 (7)	0.0118 (7)	0.0020 (6)	−0.0023 (6)	−0.0022 (5)
N2	0.0132 (7)	0.0087 (6)	0.0089 (7)	−0.0002 (5)	−0.0008 (5)	0.0004 (5)
C3	0.0114 (8)	0.0133 (8)	0.0127 (8)	0.0019 (6)	0.0016 (6)	0.0009 (6)
C4	0.0132 (8)	0.0118 (8)	0.0112 (8)	0.0021 (6)	0.0037 (6)	−0.0004 (6)
O5	0.0142 (6)	0.0283 (7)	0.0149 (7)	−0.0046 (6)	0.0038 (5)	−0.0034 (6)

Geometric parameters (Å, º)

As1—O1	1.6627 (12)	N1—H1D	0.9200
As1—O2	1.6680 (12)	N2—C4	1.482 (2)
As1—O3	1.6760 (11)	N2—C3	1.485 (2)
As1—O4	1.7264 (12)	N2—H2C	0.9200
O4—H1	0.842 (10)	N2—H2D	0.9200
C1—N1	1.488 (2)	C3—C4ii	1.517 (2)
C1—C2i	1.515 (2)	C3—H3A	0.9900
C1—H1A	0.9900	C3—H3B	0.9900
C1—H1B	0.9900	C4—C3ii	1.517 (2)
C2—N1	1.487 (2)	C4—H4A	0.9900
C2—C1i	1.515 (2)	C4—H4B	0.9900
C2—H2A	0.9900	O5—H2	0.842 (10)
C2—H2B	0.9900	O5—H3	0.836 (10)
N1—H1C	0.9200		
O1—As1—O2	112.53 (6)	C2—N1—H1D	109.2
O1—As1—O3	111.68 (6)	C1—N1—H1D	109.2
O2—As1—O3	111.44 (6)	H1C—N1—H1D	107.9
O1—As1—O4	105.86 (6)	C4—N2—C3	111.79 (12)
O2—As1—O4	107.62 (6)	C4—N2—H2C	109.3
O3—As1—O4	107.33 (6)	C3—N2—H2C	109.3
As1—O4—H1	108.0 (16)	C4—N2—H2D	109.3
N1—C1—C2i	110.60 (13)	C3—N2—H2D	109.3
N1—C1—H1A	109.5	H2C—N2—H2D	107.9
C2i—C1—H1A	109.5	N2—C3—C4ii	110.19 (13)
N1—C1—H1B	109.5	N2—C3—H3A	109.6
C2i—C1—H1B	109.5	C4ii—C3—H3A	109.6
H1A—C1—H1B	108.1	N2—C3—H3B	109.6
N1—C2—C1i	110.39 (13)	C4ii—C3—H3B	109.6
N1—C2—H2A	109.6	H3A—C3—H3B	108.1
C1i—C2—H2A	109.6	N2—C4—C3ii	110.66 (13)
N1—C2—H2B	109.6	N2—C4—H4A	109.5
C1i—C2—H2B	109.6	C3ii—C4—H4A	109.5
H2A—C2—H2B	108.1	N2—C4—H4B	109.5
C2—N1—C1	111.96 (13)	C3ii—C4—H4B	109.5
C2—N1—H1C	109.2	H4A—C4—H4B	108.1
C1—N1—H1C	109.2	H2—O5—H3	107 (2)

C1^i—C2—N1—C1	−56.31 (19)	C4—N2—C3—C4^{ii}	−56.50 (19)
C2^i—C1—N1—C2	56.43 (19)	C3—N2—C4—C3^{ii}	56.77 (19)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1···O5^{iii}	0.84 (1)	1.81 (1)	2.6492 (19)	173 (2)
N1—H1*C*···O2	0.92	1.73	2.6482 (18)	171
N1—H1*D*···O3^{iv}	0.92	1.76	2.6722 (18)	173
N2—H2*C*···O1^v	0.92	1.77	2.6788 (18)	169
N2—H2*D*···O3	0.92	1.74	2.6548 (18)	172
O5—H2···O2	0.84 (1)	1.86 (1)	2.6998 (18)	173 (2)
O5—H3···O1^{vi}	0.84 (1)	1.89 (1)	2.7065 (18)	164 (2)

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