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Piperazinium bis(dihydrogenarsenate)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.018
wR factor = 0.050
Data-to-parameter ratio = 28.1

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

The title compound, $C_4H_{12}N_2^{2+} \cdot 2H_2AsO_4^-$, contains a network of doubly protonated piperazinium cations (lying on centres of inversion) and dihydogenarsenate 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) (Fig. 1), was prepared as part of our ongoing studies of hydrogen-bonding interactions in the molecular salts of oxo-anions (Wilkinson & Harrison, 2004). Such materials show interesting crystal structures arising from the interplay of cation-to-anion N—H···O and anion-to-anion O—H···O hydrogen bonds (Lee & Harrison, 2003).

$$H_2N^+ \diagup \diagdown NH_2^+ \quad \cdot \quad 2\,(H_2AsO_4)^-$$

(I)
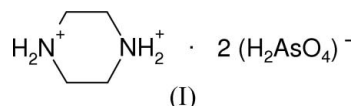
The $(H_2AsO_4)^-$ anion in (I) shows its normal tetrahedral geometry about As, with the usual distinction (Table 1) between protonated and unprotonated As—O bond lengths (Wilkinson & Harrison, 2004). The piperazinium dication lies on a centre of inversion and adopts a typical chair conformation.

As well as coulombic forces, the component species in (I) interact by way of a network of N—H···O and O—H···O hydrogen bonds (Table 2). The $(H_2AsO_4)^-$ units are linked into infinite sheets (Fig. 2) by the O—H···O hydrogen bonds. The O3—H1···O2^i interaction (see Table 2 for symmetry codes) results in centrosymmetric dimeric pairs of $(H_2AsO_4)^-$ tetrahedra linked by pairs of O—H···O hydrogen bonds. The O4—H2···O1^{ii} hydrogen bond links these dimers into an
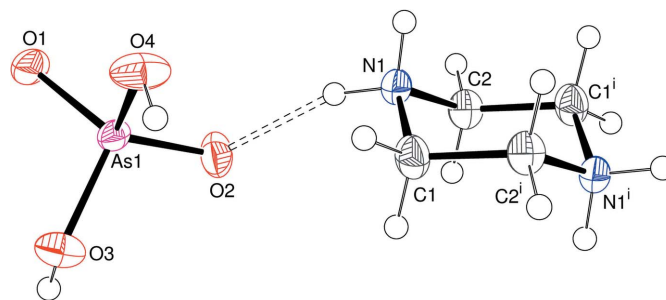
Figure 1
The molecular structure of (I) (50% displacement ellipsoids and H atoms are drawn as spheres of arbitrary radius). The hydrogen bond is indicated by a dashed line. [Symmetry code: (i) $-x$, $-y$, $1-z$.]
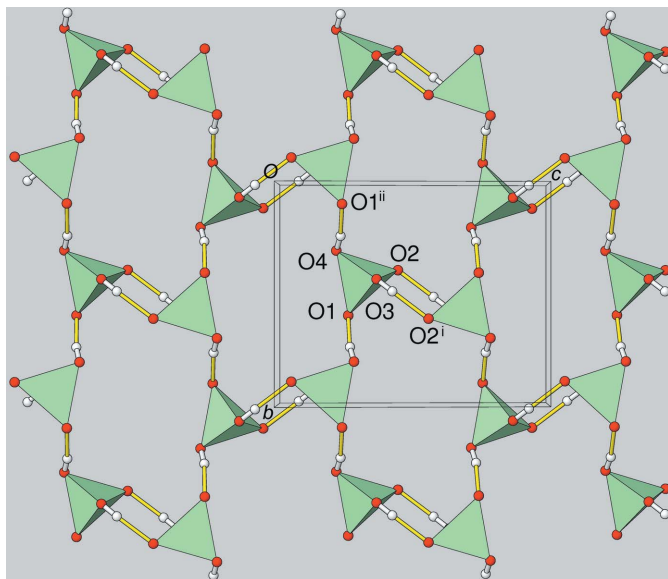
Figure 2
Detail of a part of a (100) hydrogen-bonded sheet of $(H_2AsO_4)^-$ groups in (I) in polyhedral representation, with the H$\cdots$O parts of the hydrogen bonds coloured yellow. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

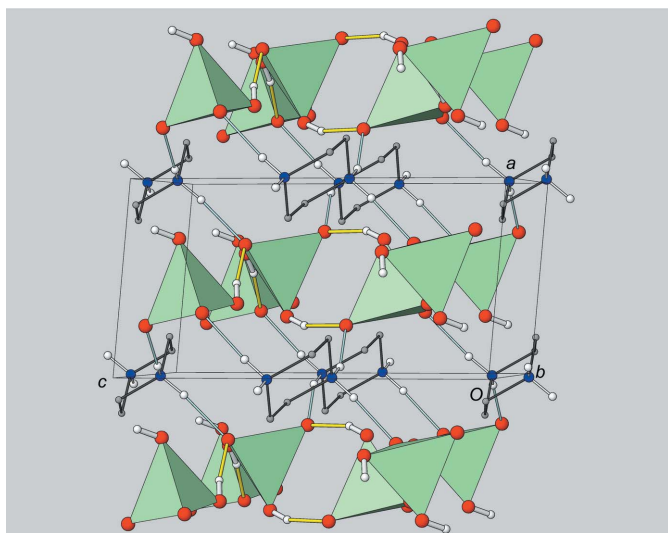**Figure 3**
The packing in (I), showing the (100) dihydrogenarsenate layers mediated by the organic cations. The H$\cdots$O parts of the N$-$H$\cdots$O and O$-$H$\cdots$O hydrogen bonds are coloured blue and yellow, respectively. H atoms bound to C atoms are omitted for clarity.

reported for guanidinium dihydrogenarsenate, $CH_6N_3\cdot H_2AsO_4$ (Wilkinson & Harrison, 2005), despite the different cation:anion ratios in the two compounds. Other ammonium hydrogenarsenate salts contain isolated pairs of tetrahedra (Todd & Harrison, 2005) or polymeric chains of anions (Wilkinson & Harrison, 2004).

Experimental

A 0.5 M aqueous piperazine solution (10 ml) was added to a 0.5 M aqueous H_3AsO_4 solution (10 ml) to give a clear solution. Crystals of (I) were obtained as the water evaporated over the course of a few days.

Crystal data

$C_4H_{12}N_2{}^{2+}\cdot 2H_2AsO_4{}^-$	$Z = 2$
$M_r = 370.02$	$D_x = 2.135$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.8208$ (3) Å	$\mu = 5.84$ mm^{-1}
$b = 8.9966$ (4) Å	$T = 293$ (2) K
$c = 11.0369$ (5) Å	Block, colourless
$\beta = 95.126$ (1)°	$0.44 \times 0.41 \times 0.22$ mm
$V = 575.66$ (5) Å^3	

Data collection

Bruker SMART1000 CCD diffractometer	5723 measured reflections
	2081 independent reflections
ω scans	1843 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$R_{int} = 0.019$
$T_{min} = 0.141$, $T_{max} = 0.277$	$\theta_{max} = 32.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0302P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$+ 0.0622P]$
$wR(F^2) = 0.050$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2081 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.061 (2)

Table 1
Selected geometric parameters (Å, °).

As1—O1	1.6633 (11)	As1—O3	1.7214 (11)
As1—O2	1.6577 (11)	As1—O4	1.7095 (11)
O1—As1—O2	115.12 (6)	O2—As1—O3	111.08 (6)
O1—As1—O3	110.51 (5)	O2—As1—O4	110.53 (6)
O1—As1—O4	106.14 (6)	O3—As1—O4	102.62 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1$\cdots$O2^i	0.83	1.82	2.6211 (16)	161
O4—H2$\cdots$O1^{ii}	0.84	1.72	2.5533 (16)	170
N1—H3$\cdots$O2	0.90	1.86	2.7163 (16)	158
N1—H4$\cdots$O1^{iii}	0.90	1.87	2.7617 (16)	173

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

infinite sheet (Fig. 3) lying parallel to (100). The As$\cdots$As^i and As$\cdots$As^{ii} separations are 4.0148 (3) and 5.0190 (3) Å, respectively. The topological connectivity of the As atoms defines a 6^3 sheet (O'Keeffe & Hyde, 1996), *i.e.* every As node participates in three polyhedral six-ring loops.

The anionic sheets are bridged by piperazinium cations, each of which participates in two N$-$H$\cdots$O interactions from each of its NH_2 groups to nearby dihydrogenarsenate tetrahedra. This results (Fig. 3) in organic and inorganic layers that alternate along the a axis. A similar layered structure has been

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H atoms bound to O atoms were found in difference Fourier maps and refined as riding on their carrier O atoms in their as-found relative positions. H atoms bound to N and C atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.90 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases.

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: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 2004); software used to prepare material for publication: *SHELXL97*.

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supporting information

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Piperazinium bis(dihydrogenarsenate)

Crystal data

$C_4H_{12}N_2^{2+} \cdot 2H_2AsO_4^-$	$F(000) = 368$
$M_r = 370.02$	$D_x = 2.135$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4016 reflections
$a = 5.8208$ (3) Å	$\theta = 2.3$–32.5°
$b = 8.9966$ (4) Å	$\mu = 5.84$ mm^{-1}
$c = 11.0369$ (5) Å	$T = 293$ K
$\beta = 95.126$ (1)°	Block, colourless
$V = 575.66$ (5) Å^3	$0.44 \times 0.41 \times 0.22$ mm
$Z = 2$	

Data collection

Bruker SMART1000 CCD diffractometer	5723 measured reflections
Radiation source: fine-focus sealed tube	2081 independent reflections
Graphite monochromator	1843 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{max} = 32.5°$, $\theta_{min} = 2.9°$
	$h = -8 \rightarrow 8$
$T_{min} = 0.141$, $T_{max} = 0.277$	$k = -8 \rightarrow 13$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.018$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.050$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.0622P]$ where $P = (F_o^2 + 2F_c^2)/3$
2081 reflections	
74 parameters	$(\Delta/\sigma)_{max} = 0.001$
0 restraints	$\Delta\rho_{max} = 0.54$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.50$ e Å^{-3}
	Extinction correction: SHELXL97, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.061 (2)

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	0.40499 (2)	0.436013 (14)	0.326653 (11)	0.01998 (6)
O1	0.32761 (19)	0.59593 (12)	0.25923 (11)	0.0300 (2)
O2	0.2595 (2)	0.39073 (14)	0.44371 (10)	0.0345 (2)
O3	0.69769 (19)	0.43297 (12)	0.36654 (11)	0.0328 (2)
H1	0.7428	0.4875	0.4244	0.039*
O4	0.3715 (2)	0.30278 (13)	0.21605 (11)	0.0369 (3)
H2	0.4733	0.2376	0.2324	0.044*
N1	0.0005 (2)	0.13912 (13)	0.43416 (10)	0.0232 (2)
H3	0.0527	0.2328	0.4280	0.028*
H4	−0.0979	0.1204	0.3684	0.028*
C1	0.1992 (2)	0.03324 (17)	0.43684 (15)	0.0276 (3)
H1A	0.3131	0.0603	0.5027	0.033*
H1B	0.2713	0.0409	0.3612	0.033*
C2	−0.1233 (2)	0.12533 (16)	0.54583 (13)	0.0258 (3)
H2A	−0.2572	0.1900	0.5393	0.031*
H2B	−0.0226	0.1564	0.6160	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.02492 (8)	0.01499 (8)	0.01921 (8)	−0.00073 (4)	−0.00256 (5)	0.00057 (4)
O1	0.0350 (5)	0.0189 (4)	0.0342 (5)	−0.0005 (4)	−0.0069 (4)	0.0071 (4)
O2	0.0452 (6)	0.0322 (6)	0.0266 (5)	−0.0180 (5)	0.0054 (5)	−0.0009 (4)
O3	0.0270 (5)	0.0352 (6)	0.0343 (6)	0.0026 (4)	−0.0070 (4)	−0.0072 (4)
O4	0.0439 (6)	0.0293 (6)	0.0342 (5)	0.0107 (5)	−0.0146 (5)	−0.0142 (4)
N1	0.0260 (5)	0.0193 (5)	0.0242 (5)	−0.0031 (4)	0.0009 (4)	0.0030 (4)
C1	0.0233 (6)	0.0267 (7)	0.0339 (7)	−0.0014 (5)	0.0095 (5)	0.0030 (5)
C2	0.0284 (6)	0.0217 (6)	0.0279 (6)	0.0011 (5)	0.0065 (5)	−0.0026 (5)

Geometric parameters (Å, º)

As1—O1	1.6633 (11)	N1—H3	0.900
As1—O2	1.6577 (11)	N1—H4	0.900
As1—O3	1.7214 (11)	C1—C2[i]	1.511 (2)
As1—O4	1.7095 (11)	C1—H1A	0.970
O3—H1	0.829	C1—H1B	0.970

O4—H2	0.842	C2—C1^i	1.511 (2)
N1—C2	1.4877 (17)	C2—H2A	0.970
N1—C1	1.4966 (18)	C2—H2B	0.970
O1—As1—O2	115.12 (6)	H3—N1—H4	108.0
O1—As1—O3	110.51 (5)	N1—C1—C2^i	111.68 (11)
O1—As1—O4	106.14 (6)	N1—C1—H1A	109.3
O2—As1—O3	111.08 (6)	C2^i—C1—H1A	109.3
O2—As1—O4	110.53 (6)	N1—C1—H1B	109.3
O3—As1—O4	102.62 (5)	C2^i—C1—H1B	109.3
As1—O3—H1	115.2	H1A—C1—H1B	107.9
As1—O4—H2	107.6	N1—C2—C1^i	110.64 (11)
C2—N1—C1	111.19 (11)	N1—C2—H2A	109.5
C2—N1—H3	109.4	C1^i—C2—H2A	109.5
C1—N1—H3	109.4	N1—C2—H2B	109.5
C2—N1—H4	109.4	C1^i—C2—H2B	109.5
C1—N1—H4	109.4	H2A—C2—H2B	108.1

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

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O3—H1⋯O2^{ii}	0.83	1.82	2.6211 (16)	161
O4—H2⋯O1^{iii}	0.84	1.72	2.5533 (16)	170
N1—H3⋯O2	0.90	1.86	2.7163 (16)	158
N1—H4⋯O1^{iv}	0.90	1.87	2.7617 (16)	173

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