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Piperazinium bis(dihydrogenarsenate)

Hazel S. Wilkinson and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

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Key indicators

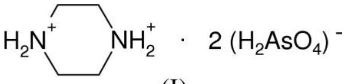
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.018
wR factor = 0.050
Data-to-parameter ratio = 28.1

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).


(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

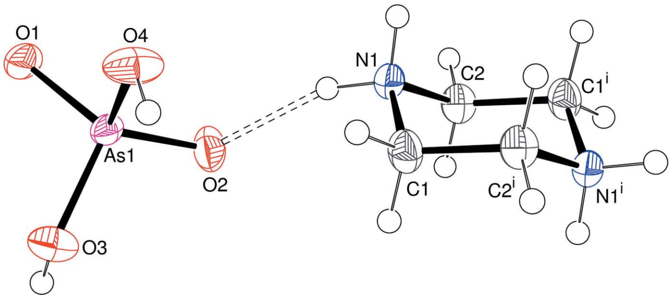


Figure 1
The molecular structure of (I) (50% displacement ellipsoids and H atoms are drawn as spheres of arbitrary radius). The hydrogen bond is indicated by a dashed line. [Symmetry code: (i) $-x$, $-y$, $1 - z$.]

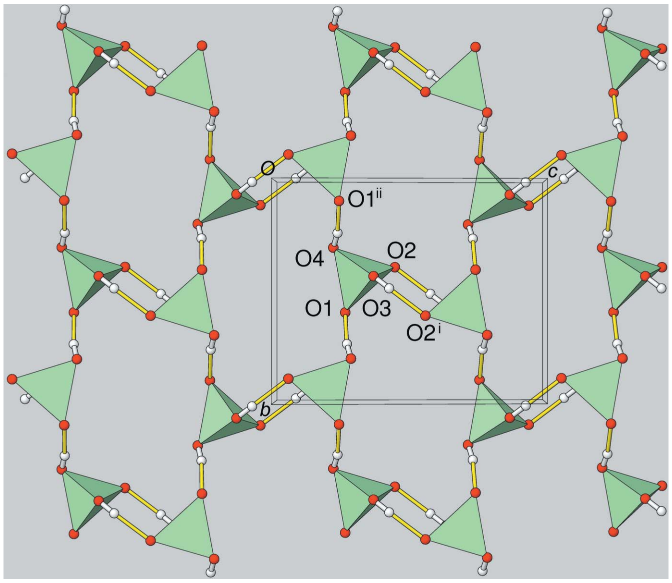


Figure 2
Detail of a part of a (100) hydrogen-bonded sheet of $(H_2AsO_4)^-$ groups in (I) in polyhedral representation, with the H$\cdots$O parts of the hydrogen bonds coloured yellow. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

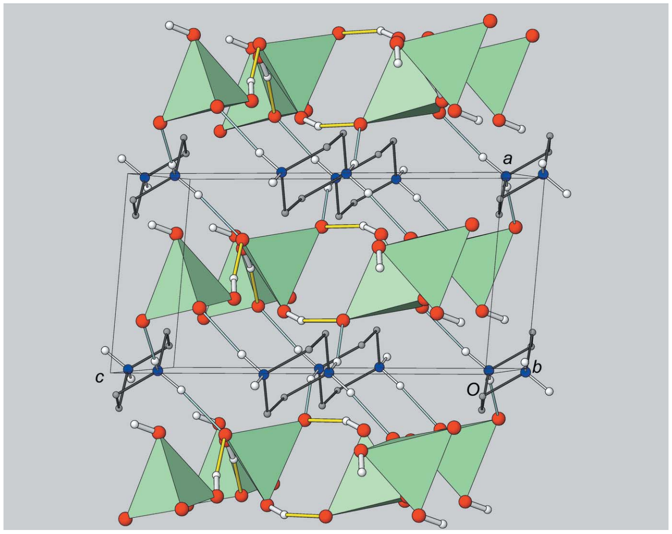


Figure 3
The packing in (I), showing the (100) dihydrogenarsenate layers mediated by the organic cations. The H$\cdots$O parts of the N—H$\cdots$O and O—H$\cdots$O hydrogen bonds are coloured blue and yellow, respectively. H atoms bound to C atoms are omitted for clarity.

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 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

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

Data collection

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.050$
$S = 1.05$
2081 reflections
74 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.0622P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}
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) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

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 $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(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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