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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.

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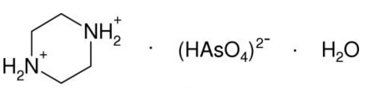
In the title compound, $C_4H_{12}N_2^{2+}\cdot HAsO_4^{2-}\cdot H_2O$, the component species interact by way of N—H$\cdots$O and O—H$\cdots$O hydrogen bonds, the latter leading to infinite sheets of $HAsO_4^{2-}$ anions and water molecules containing $R_6^6(18)$ loops. The asymmetric unit contains one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



(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.

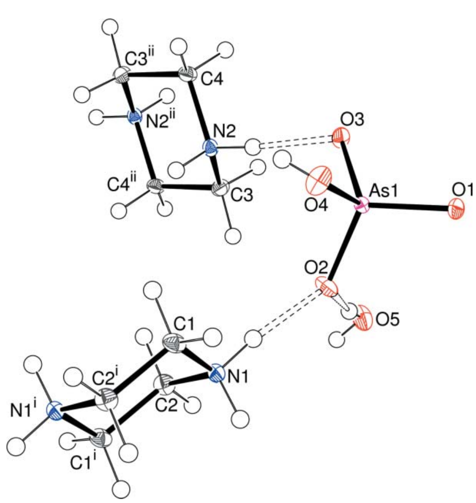


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are showwn as spheres of arbitrary radius. Hydrogen bonds are indicated by double-dashed lines. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$.]

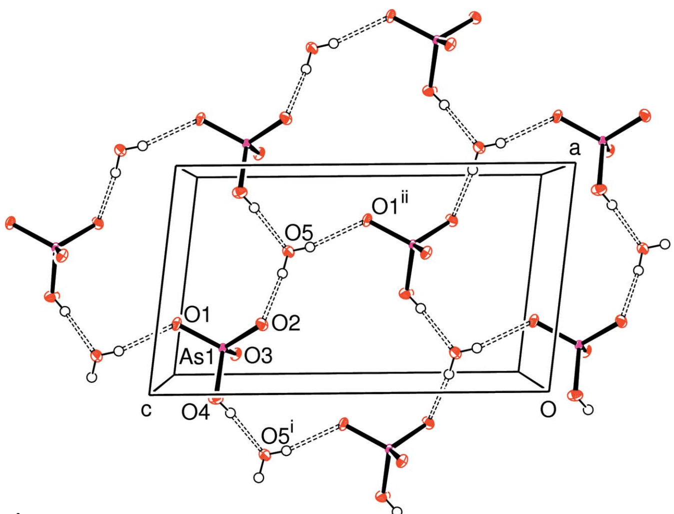


Figure 2
Detail of a part of an (010) hydrogen-bonded sheet of $HAsO_4^{2-}$ groups and water molecules in (I), with H bonds indicated by double-dashed lines. (Symmetry codes as in Table 1.)

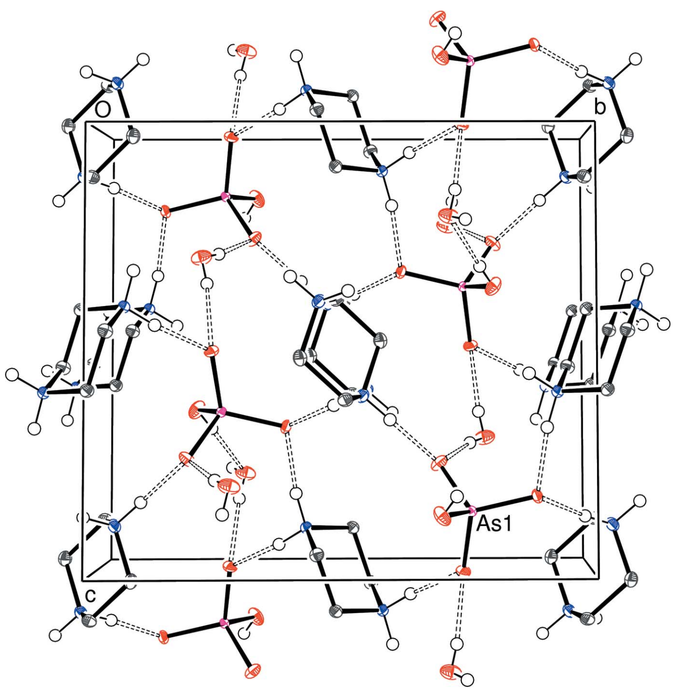


Figure 3
A view down [100] of the unit-cell packing in (I), showing the (010) hydrogenarsenate–water layers mediated by the organic cations. Hydrogen bonds are indicated by double-dashed lines and C-bound H atoms have been omitted for clarity.

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···O and N—H···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···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···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 $H_2AsO_4^-$ tetrahedra within a sheet.

Experimental

In an attempt to synthesize an analogue of $(H_3NCH_2CH_2NH_3)[AsO_2]_2$ (Lee & Harrison, 2004), aqueous solutions of piperazine (0.1 *M*) and $As^{III}{}_2O_3$ (0.1 *M*) were mixed, resulting in a colourless mixture. Translucent faceted truncated cubes of As_2O_3 recrystallized after one day. After several months, colourless slabs of (I) were dredged from the viscous liquor.

Crystal data

$C_4H_{12}N_2^{2+}\cdot HAsO_4^{2-}\cdot H_2O$
$M_r = 246.10$
Monoclinic, $P2_1/n$
$a = 6.5093$ (2) Å
$b = 12.5329$ (3) Å
$c = 11.2873$ (3) Å
$\beta = 97.0816$ (16)°
$V = 913.80$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.71$ mm^{-1}
$T = 120$ (2) K
0.40 × 0.28 × 0.14 mm

Data collection

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

Refinement

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

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

D—H···A	D—H	H···A	D···A	D—H···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}(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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