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Propane-1,3-diaminium bis(dihydrogenarsenate)

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The title compound, $(C_3H_{12}N_2)[H_2AsO_4]_2$, contains a network of propane-1,3-diaminium cations and dihydrogenarsenate anions [mean As—O = 1.682 (2) Å]. The crystal packing involves anion-to-anion O—H···O hydrogen bonds, resulting in double chains of dihydrogenarsenate tetrahedra. Cation-to-anion N—H···O hydrogen bonds generate a three-dimensional overall structure. One C atom occupies a special position with twofold symmetry.

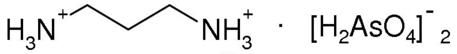
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 26.7

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

Comment

The title compound, $C_3H_{12}N_2{}^{2+}\cdot 2[H_2AsO_4)]^-$, (I), (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogen arsenates (Lee & Harrison, 2003*a*,*b*,*c*; Wilkinson & Harrison, 2004; Todd & Harrison, 2005*a*).



(I)

The $[H_2AsO_4]^-$ dihydrogenarsenate group in (I) has normal tetrahedral geometry [mean As—O = 1.682 (2) Å], with the protonated As1—O1 and As1—O2 vertices showing their expected lengthening relative to the unprotonated As1—O3 and As1—O4 bonds, which have formal partial double-bond character (Table 1). The propane-1,3-diaminium cation, which is generated by twofold symmetry from the atoms of the asymmetric unit (C2 occupies a special position with site symmetry 2), shows no unusual geometrical features.

As well as electrostatic attractions, 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 (Table 2). The $[H_2AsO_4]^-$ units are linked into polymeric

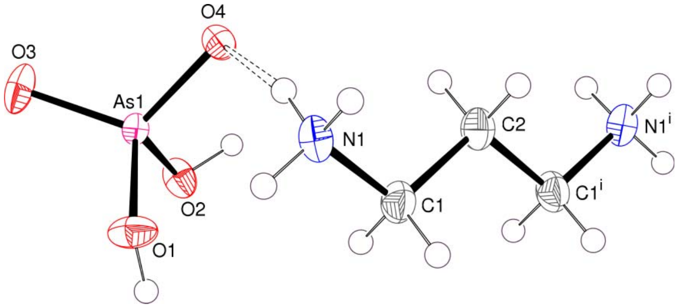


Figure 1
View of (I), showing 50% probability displacement ellipsoids (H atoms are drawn as spheres of arbitrary radii and the hydrogen bond is indicated by dashed lines). Symmetry code as in Table 1.

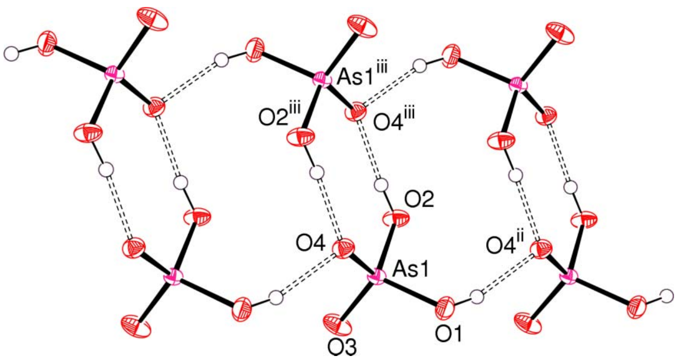


Figure 2
Detail of a hydrogen-bonded (dashed lines) dihydrogenarsenate double chain in (I). Symmetry codes as in Table 2.

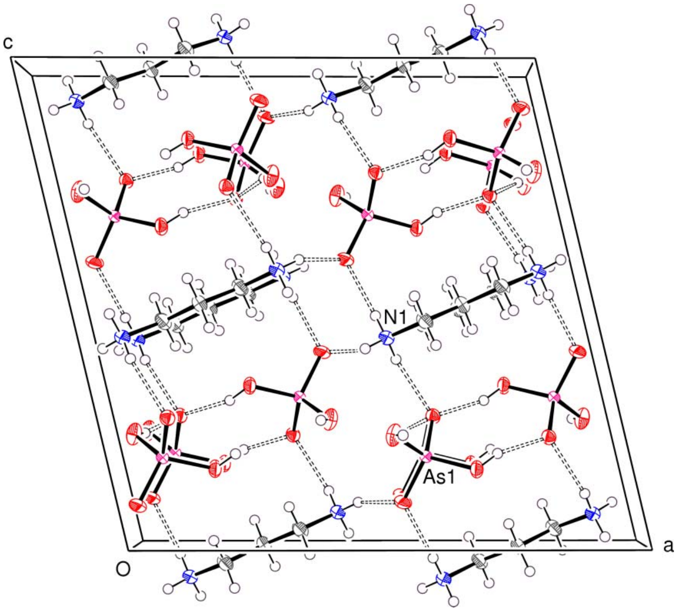


Figure 3
Projection of the unit cell contents of (I) on to (010). Dashed lines indicate hydrogen bonds.

double chains (Fig. 2) propagating along [010] by way of inversion-symmetry-generated pairs of O2—H2$\cdots$O4^{iii} and O1—H1$\cdots$O4^{ii} bonds (see Table 2 for symmetry codes). The first of these bonds results in ‘dimers’ of dihydrogenarsenate tetrahedra, which in turn are linked into double chains by the second hydrogen bond. In graph-set notation (Bernstein *et al.*, 1995), these bonding patterns correspond to $R_2^2(8)$ and $R_4^4(12)$ loops, respectively. This scheme results in every $[H_2AsO_4]^-$ group in the chain forming two hydrogen bonds to its neighbours and accepting two hydrogen bonds from its neighbours. The As$\cdots$As^{iii} (*via* O2—H2$\cdots$O4^{iii}) and As$\cdots$As^{ii} (*via* O1—H1$\cdots$O4^{ii}) separations are 4.5325 (4) and 4.6549 (4) Å, respectively (symmetry codes as in Table 2).

The organic species interacts with the dihydrogenarsenate anions by way of three N—H$\cdots$O hydrogen bonds [mean H$\cdots$O = 2.00 Å, mean N—H$\cdots$O = 158° and mean N$\cdots$O = 2.892 (3) Å], such that the [010] dihydrogenarsenate double chains are crosslinked in the *a* and *c* directions to result in a three-dimensional network (Fig. 3). A *PLATON* (Spek, 2003) analysis of (I) indicated the presence of two short C—H$\cdots$O contacts (Table 2) although their structural significance is not clear.

The hydrogen-bonded tetrahedral double chains in (I) are different from the motifs seen in related structures. In bis(cycloheptylaminium) hydrogenarsenate monohydrate (Todd & Harrison, 2005*a*) and bis(benzylammonium) hydrogenarsenate monohydrate (Lee & Harrison, 2003*c*), hydrogen-bonded dimers of $[HAsO_4]^{2-}$ units occur, with the dimers bridged into double chains by intervening water molecules. In piperidinum dihydrogenarsenate (Lee & Harrison, 2003*b*) and *t*-butylammonium dihydrogenarsenate (Wilkinson & Harrison, 2004), single chains of $[H_2AsO_4]^-$ anions occur with each adjacent dihydrogenarsenate pair linked by a pair of hydrogen bonds. In propane-1,3-diaminium hydrogenarsenate monohydate (Todd & Harrison, 2005*b*), containing the same cation as (I) but prepared at higher pH, yet another hydrogen-bonded chain motif occurs.

Experimental

0.5 *M* aqueous propane-1,3-diamine solution (10 ml) was added to 0.5 *M* aqueous H_3AsO_4 solution (10 ml) to result in a clear solution. A mass of plate- and slab-like crystals of (I) grew as the water evaporated over the course of a few days.

Crystal data

$(C_3H_{12}N_2)[AsH_2O_4]_2$
$M_r = 358.02$
Monoclinic, $I2/a$
$a = 15.5563$ (8) Å
$b = 4.6549$ (2) Å
$c = 15.0454$ (7) Å
$\beta = 103.399$ (1)°
$V = 1059.83$ (9) Å^3
$Z = 4$

$D_x = 2.244$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3458 reflections
$\theta = 2.7$–32.5°
$\mu = 6.33$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.50 × 0.19 × 0.03 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.144$, $T_{max} = 0.833$
5128 measured reflections

1899 independent reflections
1667 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 32.5°$
$h = -23 \rightarrow 23$
$k = -7 \rightarrow 5$
$l = -22 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 1.02$
1899 reflections
71 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -1.49$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0037 (6)

Table 1
Selected geometric parameters (Å, °).

As1—O3	1.6375 (17)	As1—O1	1.7071 (17)
As1—O4	1.6669 (16)	As1—O2	1.7180 (18)
N1—C1—C2—C1^i	179.5 (3)		

Symmetry code: (i) $-x + \frac{3}{2}, y, -z + 1$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4$^{\rm ii}$	0.83	1.82	2.608 (3)	159
O2—H2···O4$^{\rm iii}$	0.90	1.74	2.603 (3)	161
N1—H3···O3$^{\rm iv}$	0.89	1.89	2.740 (3)	160
N1—H4···O4	0.89	2.13	2.967 (3)	156
N1—H5···O3$^{\rm v}$	0.89	1.97	2.818 (3)	158
C1—H7···O2$^{\rm vi}$	0.97	2.48	3.389 (3)	156
C2—H8···O2$^{\rm v}$	0.97	2.52	3.482 (3)	174

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

The *I*-centred unit cell was chosen in preference to the *C*-centred setting (space group *C*2/*c*) to avoid a very obtuse β angle of 127° (Mighell, 2003). The O-bound H atoms were found in difference maps and refined as riding on their carrier O atoms in their as-found relative positions. H atoms bonded to C and N atoms were placed in idealized positions (C—H = 0.97 Å and N—H = 0.89 Å) and refined as riding, allowing for free rotation of the $-NH_3$ group. The constraint $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier) was applied in all cases. The highest difference peak is 0.95 Å from O3 and the deepestdifference hole is 1.20 Å from As1.

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); software used to prepare material for publication: *SHELXL97*.

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