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Key indicators

 Single-crystal X-ray study
 $T = 293$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 Disorder in main residue
 R factor = 0.029
 wR factor = 0.074
 Data-to-parameter ratio = 29.0

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

2-Methylpiperazinium bis(dihydrogenarsenate)

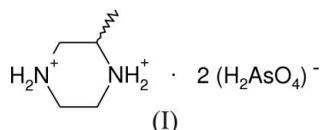
The title compound, $\text{C}_5\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{H}_2\text{AsO}_4^-$, contains a network of centrosymmetric doubly protonated 2-methylpiperazinium cations, showing disorder of the methyl group, accompanied by dihydrogenarsenate anions. The component species interact by way of cation-to-anion $\text{N}-\text{H} \cdots \text{O}$ and anion-to-anion $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, the latter leading to infinite sheets of the H_2AsO_4^- anions containing $R_6^6(24)$ supramolecular loops.

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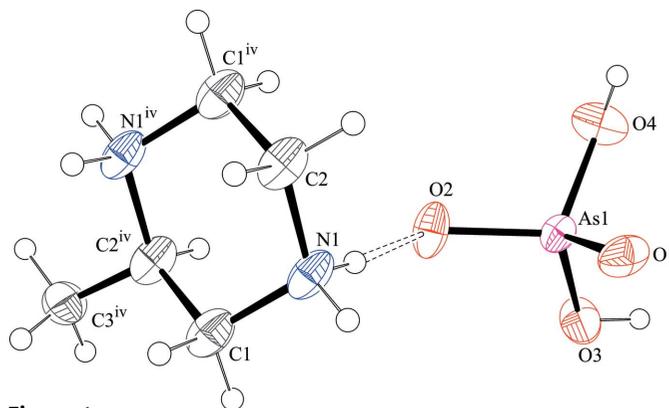
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Comment

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, 2007).



The tetrahedral H_2AsO_4^- anion in (I) [mean $\text{As}-\text{O} = 1.677$ (2) Å], shows the usual distinction (Table 1) between protonated and unprotonated $\text{As}-\text{O}$ bond lengths (Wilkinson & Harrison, 2007). The complete 2-methylpiperazinium dication is generated by inversion. This must result in disorder, as each dication is chiral at C2. Thus, the two enantiomers are superimposed in the long-range structure of the crystal, with all the atoms of the ring overlapped. A typical chair conformation for the six-membered ring arises, and atom C3 of the methyl group is equatorial to the ring in both disorder components.


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 double-dashed line. Only one disorder component of the cation is shown. [Symmetry code: (iv) $-x, -y, 1 - z$.]

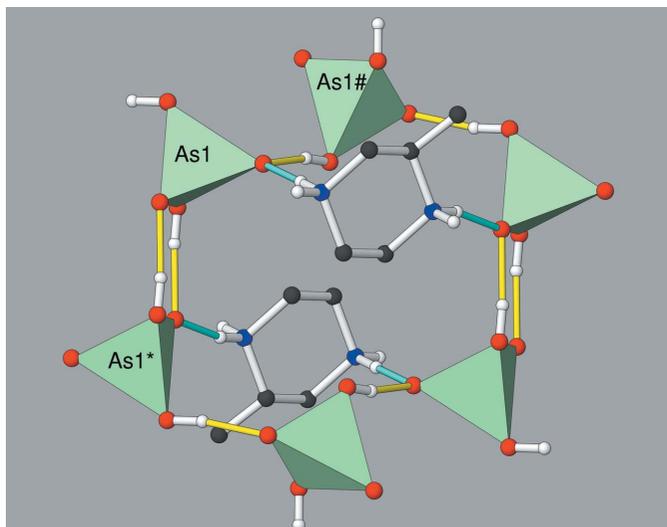


Figure 2

Detail of a six-membered ring of H_2AsO_4^- groups in (I), in polyhedral representation, with attached organic cations. Only one disorder component of each cation is shown and the C-bound H atoms are omitted for clarity. The $\text{H}\cdots\text{O}$ parts of the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are coloured yellow and the $\text{H}\cdots\text{O}$ parts of the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are light blue. The As1^* and $\text{As1}^\#$ tetrahedra are generated by the symmetry operations $(1-x, 1-y, 1-z)$ and $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, respectively.

As well as Coulombic forces, the component species in (I) interact by way of a network of anion-to-anion $\text{O}-\text{H}\cdots\text{O}$ and cation-to-anion $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). The hydrogen-bonding scheme and overall structure in (I) are very similar to those in piperazinium bis(dihydrogenarsenate), (II) (Wilkinson & Harrison, 2007). In both (I) and (II), the H_2AsO_4^- units are linked into infinite (100) layers by the $\text{O}-\text{H}\cdots\text{O}$ bonds. A distinctive feature of the sheets are supra-molecular $R_6^0(24)$ rings (Bernstein *et al.*, 1995) built up from six tetrahedra, the rings being stabilized by $\text{N}-\text{H}\cdots\text{O}$ bonds from the organic cations (Fig. 2). For the two inter-tetrahedral $\text{O}-\text{H}\cdots\text{O}$ interactions, the $\text{As}\cdots\text{As}^i$ and $\text{As}\cdots\text{As}^{ii}$ (see Table 2 for symmetry codes) separations for (I) are 4.3061 (3) and 4.7599 (3) Å, respectively, which are distinctly different from the values of 4.0148 (3) and 5.0190 (3) Å for the topologically equivalent network in (II).

Experimental

To an aqueous racemic 2-methylpiperazine solution (10 ml, 0.5 M) was added an aqueous H_3AsO_4 solution (10 ml, 0.5 M), resulting in a clear solution. Chunks and blocks of (I) grew as the water evaporated over the course of a few days; these were harvested by vacuum filtration and rinsed with acetone.

Crystal data

$\text{C}_5\text{H}_{14}\text{N}_2^{2+}\cdot 2\text{AsH}_2\text{O}_4^-$	$V = 669.31 (5) \text{ \AA}^3$
$M_r = 384.06$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.7537 (3) \text{ \AA}$	$\mu = 5.02 \text{ mm}^{-1}$
$b = 8.1753 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 12.7105 (5) \text{ \AA}$	$0.37 \times 0.12 \times 0.03 \text{ mm}$
$\beta = 107.501 (2)^\circ$	

Data collection

Bruker SMART 1000 CCD diffractometer	6913 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	2409 independent reflections
$T_{\min} = 0.258, T_{\max} = 0.864$	1929 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	83 parameters
$wR(F^2) = 0.074$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\max} = 0.65 \text{ e \AA}^{-3}$
2409 reflections	$\Delta\rho_{\min} = -0.67 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

As1—O1	1.6477 (16)	As1—O3	1.6974 (16)
As1—O2	1.6531 (16)	As1—O4	1.7082 (17)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O4—H2 \cdots O1 ⁱ	0.84	1.76	2.599 (3)	174
O3—H1 \cdots O2 ⁱⁱ	0.86	1.70	2.548 (2)	169
N1—H4 \cdots O2	0.90	1.79	2.689 (2)	175
N1—H3 \cdots O1 ⁱⁱⁱ	0.90	1.80	2.685 (2)	168

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

The C3 methyl group is disordered over two positions in the molecule. Crystal symmetry dictates equal occupancy for both components. The O-bound H atoms were found in a difference map and refined as riding in their as-found relative positions, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ (see Table 2 for distances). The C- and N-bonded H atoms were placed in idealized positions ($\text{C}-\text{H} = 0.96\text{--}0.97 \text{ \AA}$ and $\text{N}-\text{H} = 0.90 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The methyl group was allowed to rotate, but not to tip, to best fit the electron density.

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

Acta Cryst. (2007). E63, m900–m901 [https://doi.org/10.1107/S1600536807008392]

2-Methylpiperazinium bis(dihydrogenarsenate)

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2-Methylpiperazinium bis(dihydrogenarsenate)

Crystal data

$C_5H_{14}N_2^{2+} \cdot 2AsH_2O_4^-$

$M_r = 384.06$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.7537$ (3) Å

$b = 8.1753$ (4) Å

$c = 12.7105$ (5) Å

$\beta = 107.501$ (2)°

$V = 669.31$ (5) Å³

$Z = 2$

$F(000) = 384$

$D_x = 1.906$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3599 reflections

$\theta = 3.0$ – 32.5 °

$\mu = 5.02$ mm⁻¹

$T = 293$ K

Blade, colourless

$0.37 \times 0.12 \times 0.03$ mm

Data collection

Bruker SMART1000 CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 1999)

$T_{\min} = 0.258$, $T_{\max} = 0.864$

6913 measured reflections

2409 independent reflections

1929 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 3.0$ °

$h = -10 \rightarrow 8$

$k = -12 \rightarrow 10$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.074$

$S = 1.06$

2409 reflections

83 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difmap and geom

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.65$ e Å⁻³

$\Delta\rho_{\min} = -0.67$ e Å⁻³

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
As1	0.42568 (3)	0.44828 (2)	0.649888 (15)	0.02836 (7)	
O1	0.2951 (3)	0.5701 (2)	0.54973 (14)	0.0430 (4)	
O2	0.3233 (3)	0.2636 (2)	0.64397 (13)	0.0431 (4)	
O3	0.4450 (3)	0.5192 (3)	0.77811 (14)	0.0495 (5)	
H1	0.5209	0.6055	0.7961	0.059*	
O4	0.6781 (3)	0.4345 (2)	0.65004 (14)	0.0484 (5)	
H2	0.6918	0.4387	0.5862	0.058*	
N1	-0.0381 (3)	0.1715 (2)	0.49849 (15)	0.0382 (4)	
H3	-0.1195	0.2590	0.4734	0.046*	
H4	0.0794	0.2070	0.5480	0.046*	
C1	-0.1470 (4)	0.0578 (3)	0.5536 (2)	0.0432 (5)	
H1A	-0.2786	0.0251	0.5020	0.052*	
H1B	-0.1750	0.1127	0.6153	0.052*	
C2	0.0139 (4)	0.0927 (3)	0.40532 (19)	0.0411 (5)	
H2A	-0.1125	0.0613	0.3489	0.049*	
H2B	0.0893	0.1687	0.3730	0.049*	0.50
C3	0.1037 (8)	0.2083 (7)	0.3563 (4)	0.0443 (11)	0.50
H3A	0.0336	0.3109	0.3543	0.067*	0.50
H3B	0.0931	0.1746	0.2825	0.067*	0.50
H3C	0.2473	0.2204	0.3979	0.067*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.03332 (12)	0.02582 (11)	0.02342 (10)	0.00174 (8)	0.00472 (7)	-0.00104 (7)
O1	0.0517 (10)	0.0406 (9)	0.0385 (8)	0.0223 (7)	0.0163 (7)	0.0131 (7)
O2	0.0483 (9)	0.0289 (8)	0.0387 (8)	-0.0048 (7)	-0.0073 (7)	0.0019 (6)
O3	0.0695 (12)	0.0511 (11)	0.0351 (8)	-0.0228 (9)	0.0264 (8)	-0.0164 (8)
O4	0.0333 (8)	0.0767 (14)	0.0329 (8)	0.0071 (8)	0.0064 (6)	0.0050 (8)
N1	0.0386 (9)	0.0284 (8)	0.0367 (9)	0.0113 (7)	-0.0051 (7)	-0.0046 (8)
C1	0.0461 (13)	0.0352 (12)	0.0418 (12)	0.0095 (9)	0.0034 (10)	-0.0039 (10)
C2	0.0478 (13)	0.0351 (10)	0.0324 (10)	0.0093 (9)	-0.0002 (9)	-0.0013 (9)
C3	0.054 (3)	0.041 (3)	0.047 (3)	-0.001 (2)	0.027 (2)	0.006 (2)

Geometric parameters (\AA , $^\circ$)

As1—O1	1.6477 (16)	C1—C2 ⁱ	1.520 (3)
As1—O2	1.6531 (16)	C1—H1A	0.9700
As1—O3	1.6974 (16)	C1—H1B	0.9700
As1—O4	1.7082 (17)	C2—C3	1.370 (5)

O3—H1	0.8619	C2—C1 ⁱ	1.520 (3)
O4—H2	0.8442	C2—H2A	0.9700
N1—C2	1.480 (3)	C2—H2B	0.9700
N1—C1	1.485 (3)	C3—H3A	0.9600
N1—H3	0.9000	C3—H3B	0.9600
N1—H4	0.9000	C3—H3C	0.9600
O1—As1—O2	113.42 (9)	H1A—C1—H1B	108.2
O1—As1—O3	113.84 (10)	C3—C2—N1	107.9 (3)
O2—As1—O3	105.42 (9)	C3—C2—C1 ⁱ	114.7 (3)
O1—As1—O4	110.05 (9)	N1—C2—C1 ⁱ	109.62 (19)
O2—As1—O4	110.11 (9)	C3—C2—H2A	104.9
O3—As1—O4	103.47 (9)	N1—C2—H2A	109.9
As1—O3—H1	113.7	C1 ⁱ —C2—H2A	109.7
As1—O4—H2	113.2	N1—C2—H2B	110.0
C2—N1—C1	112.03 (18)	C1 ⁱ —C2—H2B	109.4
C2—N1—H3	109.2	H2A—C2—H2B	108.2
C1—N1—H3	109.2	C2—C3—H3A	109.5
C2—N1—H4	109.2	H2B—C3—H3A	120.5
C1—N1—H4	109.2	C2—C3—H3B	109.5
H3—N1—H4	107.9	H2B—C3—H3B	108.4
N1—C1—C2 ⁱ	110.1 (2)	H3A—C3—H3B	109.5
N1—C1—H1A	109.6	C2—C3—H3C	109.5
C2 ⁱ —C1—H1A	109.6	H2B—C3—H3C	98.9
N1—C1—H1B	109.6	H3A—C3—H3C	109.5
C2 ⁱ —C1—H1B	109.6	H3B—C3—H3C	109.5
C2—N1—C1—C2 ⁱ	57.8 (3)	C1—N1—C2—C1 ⁱ	-57.5 (3)
C1—N1—C2—C3	177.0 (3)		

Symmetry code: (i) $-x, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H2 \cdots O1 ⁱⁱ	0.84	1.76	2.599 (3)	174
O3—H1 \cdots O2 ⁱⁱⁱ	0.86	1.70	2.548 (2)	169
N1—H4 \cdots O2	0.90	1.79	2.689 (2)	175
N1—H3 \cdots O1 ^{iv}	0.90	1.80	2.685 (2)	168

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, y+1/2, -z+3/2$; (iv) $-x, -y+1, -z+1$.