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Bis(cycloheptylaminium) hydrogenarsenate monohydrate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.028
wR factor = 0.068
Data-to-parameter ratio = 21.3

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

The title compound, $2C_7H_{16}N^+\cdot HAsO_4^{2-}\cdot H_2O$, contains a network of cycloheptylaminium cations, hydrogenarsenate anions and water molecules. The crystal packing involves N—H···O [average H···O = 1.86 Å, N—H···O = 172° and N···O = 2.756 (2) Å] and O—H···O [average H···O = 1.91 Å, O—H···O = 168° and O···O = 2.756 (2) Å] hydrogen bonds, resulting in a layered structure.

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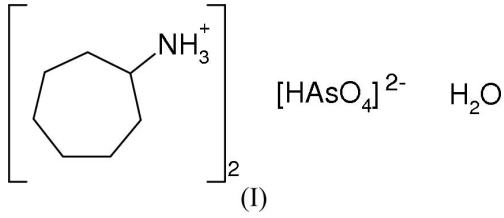
Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing studies of hydrogen-bonding interactions in the crystal structures of (protonated) amine phosphates (Demir *et al.*, 2003), phosphites (Harrison, 2003), selenites (Ritchie & Harrison, 2003) and arsenates (Lee & Harrison, 2003*a*,*b*,*c*; Wilkinson & Harrison, 2004).



(I)

The crystal structure of (I) contains two unique $C_7H_{15}N^+$ cycloheptylaminium cations, one unique $HAsO_4^{2-}$ hydrogen-

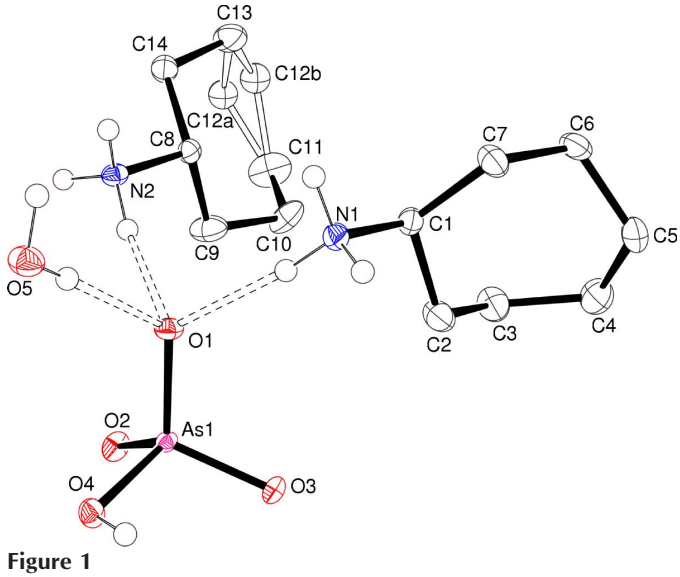


Figure 1
Asymmetric unit of (I), showing 50% displacement ellipsoids (arbitrary spheres for H atoms; C-bound H atoms have been omitted for clarity). Hydrogen bonds are indicated by dashed lines. Both disorder components are shown.

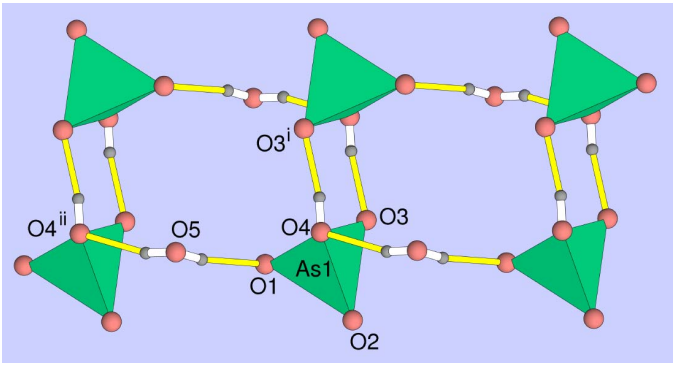


Figure 2
Detail of a hydrogen-bonded hydrogenarsenate/water chain in (I). Colour key: $[HAsO_4]^{2-}$ tetrahedra: green; O atoms: pink; H atoms: grey. The H···O portions of the hydrogen bonds are highlighted in yellow. Symmetry labels as in Table 2.

arsenate anion and one unique water molecule. The geometric parameters for the organic species are unexceptional. One of the C atoms of the C8-containing cation is disordered over two adjacent sites (see *Experimental*). The conformation of the C atoms of the undisordered (C1-containing) ring is close to a twist–chair (the predicted lowest-energy conformation for a seven-membered ring; Hendrickson, 1967) with a pseudo-twofold axis passing through C4 and the C1—C7 bond mid-point. The $HAsO_4^{2-}$ group in (I) shows its standard (Lee & Harrison, 2003) tetrahedral geometry [average As—O = 1.691 (2) Å], with the protonated As—O4 vertex showing its expected lengthening relative to the other As—O bonds.

As well as electrostatic attractions, the component species in (I) interact by means of a network of N—H···O and O—H···O hydrogen bonds (Table 2). The $HAsO_4^{2-}$ units and the water molecules (O5/H2/H3) are linked into a polymeric chain in the [010] direction by hydrogen bonds (Fig. 2). Inversion symmetry generates linked pairs of $HAsO_4^{2-}$ units (by way of two O4—H1···O3 bonds), which are in turn bridged by pairs of water molecules into a chain. The same chain motif occurs in bis(benzylaminium) hydrogenarsenate monohydrate (Lee & Harrison, 200*c*) but is different from that seen in propane-1,2-diaminium hydrogenarsenate monohydrate (Lee & Harrison, 2003*a*).

The organic species interact with the hydrogenarsenate/water chains by way of N—H···O hydrogen bonds (Table 2). All six of the $-NH_3^+$ H atoms are involved in these links [average H···O = 1.86 Å, N—H···O = 172° and N···O = 2.756 (2) Å]. Five of the acceptor O atoms are parts of $HAsO_4^{2-}$ species and one is part of a water molecule. This hydrogen-bonding scheme results in (101) hydrogenarsenate/water/ammonium layers sandwiched between the cycloheptyl moieties (Fig. 3), which interact in turn by way of van der Waals forces.

Experimental

A 0.5 *M* cycloheptylamine solution (10 ml) in cyclohexane was layered on top of a 0.5 *M* aqueous H_3AsO_4 solution (10 ml) and covered to prevent solvent evaporation. A mass of block-like crystals of (I) grew at the interface of the solvent layers over the course of a few days.

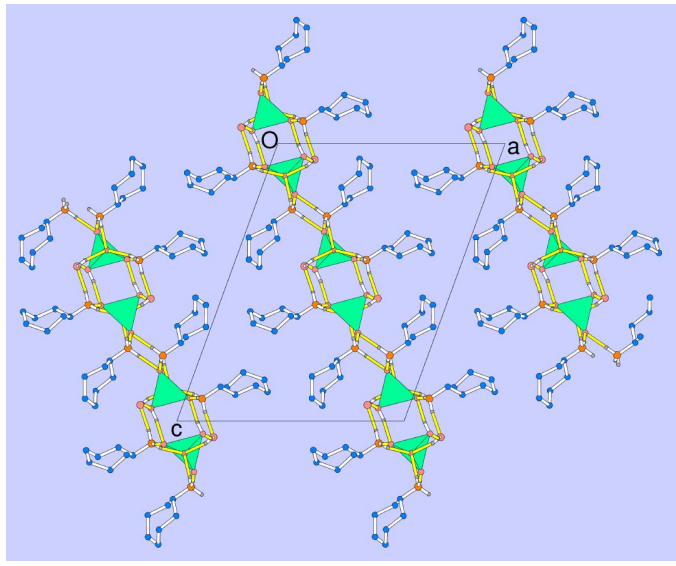


Figure 3
[010] projection of the unit cell packing for (I). Colour key as in Fig. 2; additionally, C atoms: blue; N atoms: orange. C-bound H atoms have been omitted for clarity.

Crystal data

$2C_7H_{16}N^+\cdot HAsO_4^{2-}\cdot H_2O$
M_r = 386.36
Monoclinic, $P2_1/n$
a = 15.5003 (4) Å
b = 6.4005 (1) Å
c = 20.1552 (5) Å
β = 110.0396 (11)°
V = 1878.53 (7) Å^3
Z = 4
D_x = 1.366 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4402 reflections
θ = 2.9–27.5°
μ = 1.83 mm^{-1}
T = 120 (2) K
Block, colourless
0.48 × 0.14 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.473, T_{max} = 0.810
17 560 measured reflections
4294 independent reflections
3604 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.6°
$h = -15 \rightarrow 20$
$k = -8 \rightarrow 7$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.068
S = 1.04
4294 reflections
202 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 1.7751P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0027 (3)

Table 1
Selected interatomic distances (Å).

As1—O2	1.6644 (13)	As1—O1	1.6789 (13)
As1—O3	1.6732 (13)	As1—O4	1.7466 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H1···O3^{i}	0.87	1.77	2.6250 (19)	169
O5—H2···O4^{ii}	0.89	2.00	2.865 (2)	165
O5—H3···O1	0.83	1.96	2.779 (2)	171
N1—H4···O3^{ii}	0.91	1.83	2.735 (2)	175
N1—H5···O5^{iii}	0.91	1.90	2.805 (2)	173
N1—H6···O1	0.91	1.87	2.762 (2)	166
N2—H20···O1	0.91	1.91	2.794 (2)	165
N2—H21···O2^{iv}	0.91	1.84	2.744 (2)	177
N2—H22···O2^{ii}	0.91	1.79	2.697 (2)	173

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

Atom C12 is disordered over two adjacent sites [C12*a*···C12*b* = 0.606 (5) Å]. The two components were refined isotropically, together with a population ratio of 0.662 (15):0.338 (15). The O-bound H atoms were found in difference maps and refined as riding in their as-found relative positions (Table 2). The H atoms bonded to C and N atoms were placed in idealized positions [C—H = 0.99 and 1.00 Å, and N—H = 0.91 Å] and refined as riding, allowing for free rotation of the rigid –NH_3 groups about the C—N bonds. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) was applied in all cases.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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, 1999); software used to prepare material for publication: *SHELXL97*.

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