catena-Poly[[[dichlorido(pyridin-1-ium-3-yl)arsenic(III)]-*μ*-chlorido] mono-hydrate]

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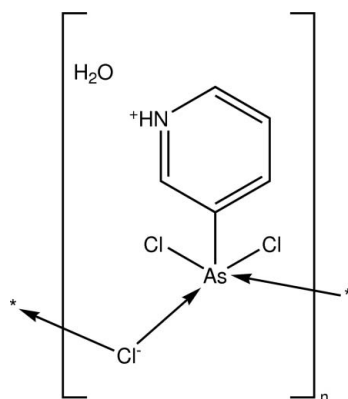
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The crystal structure of the title compound, $\{[AsCl_3(C_5H_5N)]\cdot H_2O\}_n$, is characterized by polymeric chains consisting of alternating arsenic and chlorine atoms running parallel to the *a* axis. O—H⋯Cl and N—H⋯O hydrogen bonds mediated by non-coordinating water molecules assemble these chains into a three-dimensional framework. The As^{III} atom, the atoms of the pyridinium ring and the water O atom have *m* site symmetry and the bridging Cl atom has site symmetry 2. This is the first reported organotrichloroarsenate(III) in which arsenic adopts a ψ-octahedral fivefold coordination.

Related literature

For the synthesis, see: Binz & von Schickh (1936). For monomeric and oligomeric monoorganohaloarsenates(III) with tetracoordinate arsenic, see: Grewe *et al.* (1998). For homologous monoorganohaloantimonate(III)/-bismuthate(III) structures, see: Althaus *et al.* (1999); Breunig *et al.* (1992, 1999, 2010); Hall & Sowerby (1988); James *et al.* (1999); Preut *et al.* (1987); Sheldrick & Martin (1992); von Seyerl *et al.* (1986). For organoarsenic functionalized metal oxide clusters, see: Breen, Clérac *et al.* (2012); Breen, Zhang *et al.* (2012); Onet *et al.* (2011); Zhang *et al.* (2012).

Experimental

Crystal data

$[AsCl_3(C_5H_5N)]\cdot H_2O$	$V = 930.37$ (17) Å³
$M_r = 278.39$	$Z = 4$
Orthorhombic, $Im2a$	Mo $K\alpha$ radiation
$a = 8.2107$ (9) Å	$\mu = 4.46$ mm⁻¹
$b = 8.5812$ (9) Å	$T = 200$ K
$c = 13.2046$ (14) Å	$0.5 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD diffractometer	3423 measured reflections
	1184 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	1167 reflections with $I > 2\sigma(I)$
$T_{min} = 0.341$, $T_{max} = 0.469$	$R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	
$S = 1.10$	$\Delta\rho_{max} = 1.14$ e Å⁻³
1184 reflections	$\Delta\rho_{min} = -1.28$ e Å⁻³
66 parameters	Absolute structure: Flack (1983), 529 Friedel pairs
3 restraints	Flack parameter: 0.006 (12)

Table 1
Selected bond lengths (Å).

As1—Cl1	2.2624 (8)	As1—Cl2	2.8907 (5)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯Cl2	0.82 (2)	2.40 (2)	3.197 (2)	165 (3)
N3—H3⋯O1^i	0.88	1.84	2.711	173

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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metal-organic compounds

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supporting information

catena-Poly[[[dichlorido(pyridin-1-ium-3-yl)arsenic(III)]-*μ*-chlorido] monohydrate]

Lukas Reck and Wolfgang Schmitt

S1. Comment

In the course of our work on arylarsonate functionalized metal oxide clusters (see Breen, Clérac *et al.* (2012), Breen, Zhang *et al.* (2012) and references therein for vanadium oxide clusters, Onet *et al.* (2011) for molybdenum oxide clusters and Zhang *et al.* (2012) for manganese oxide clusters) we prepared the title compound, whose crystal structure had until now not been determined. In general, the structural chemistry of organohaloarsenates(III) has not been the object of intense study, the only relevant peer-reviewed publication known to us being the contribution by Grewe *et al.* (1998), which is summarized below. The homologous organohalobismuthates(III) and organohaloantimonates(III) have been more widely studied.

Organodichloroarsines compounds are known to act as soft Lewis acids and form adducts with chloride anions, *e.g.* $[RAsCl_3]^-$ (R = Me, Et, Ph) and $[MeAsCl_2(\mu\text{-Cl})AsCl_2Me]^-$. In these adducts, arsenic occurs in ψ-trigonal bipyramidal fourfold coordination. Pentacoordinate, ψ-octahedral adducts are only known for the bromo analogues on account of their stronger acidity: organotribromoarsenates(III) form doubly bridged dimers $[RBr_2As(\mu\text{-Br}_2)AsBr_2R]^{2-}$ (R = Me, Et, Ph) (Grewe *et al.*, 1998). The homologous organohaloantimonates(III) and organohalobismuthates(III) form a wider variety of structures based mostly on ψ-octahedral REX_4 motifs. These units are found isolated in $[PhSbCl_4]^{2-}$ (Hall & Sowerby, 1988), $[PhSbBr_4]^{2-}$ (James *et al.*, 1999) and $[MeSbI_4]^{2-}$ (Breunig *et al.*, 1992). The ψ-trigonal bipyramidal $[PhSbCl_3]^-$ does exist (Hall & Sowerby, 1988), but its ψ-octahedral dimer $[PhCl_2Sb(\mu\text{-Cl})_2SbCl_2Ph]^{2-}$ is also attested (Preut *et al.*, 1987). $[Me_2Sb_2Cl_6]^{2-}$ (Breunig *et al.*, 2010), $[Me_2Sb_2Br_6]^{2-}$ (Althaus *et al.*, 1999), $[Ph_2Sb_2I_6]^{2-}$ (Breunig *et al.*, 1999) and $[Ph_2Bi_2Br_6]^{2-}$ (James *et al.*, 1999) form analogous structures. Addition of a further halide ion results in structures of the $[RX_3E(\mu\text{-}X)EX_3R]^{3-}$ type such as $[Ph_2Sb_2Cl_7]^{3-}$ and $[Ph_2Sb_2Br_7]^{3-}$ (Sheldrick & Martin, 1992). The highest aggregation is found in $[\{PhSbI(\mu^2\text{-I})\}_4(\mu^4\text{-I})]^-$ (von Seyerl *et al.*, 1986), which features an I_4 square with Sb atoms on the edges and another I atom in the centre of the square. In all organohaloarsenate(III), -antimonate(III) and -bismuthate(III) structures, bonds to bridging halide ligands are considerably longer than bonds to terminal halide ligands and bridging halide ligands are coordinated *cis* to one another.

In the title compound, the acidity of the aryldichloroarsine is enhanced by the electron-withdrawing, positively charged pyridinio substituent, so that a ψ-octahedral structure similar to the one encountered in $[RBr_2As(\mu\text{-Br}_2)AsBr_2R]^{2-}$ or $[PhCl_2Sb(\mu\text{-Cl})_2SbCl_2Ph]^{2-}$ becomes possible: As is coordinated axially to the organic substituent and equatorially to four chloride ligands, two bridging and two terminal. The terminal chloride ligands are located *cis* to one another and connected to As by short bonds, while the bridging chloride ligands are much more distant from the As centre. In contrast to in the compounds cited above, these bridging chloride ligands do not link to the same organoarsenic unit, but to two different arsenic atoms, thus forming a polymeric chain running along the crystallographic *a* axis (*cf.* Figure 1).

   The nitrogen atom on the pyridine ring forms an N—H⋯O hydrogen bond to a co-crystallized water molecule. The two O—H bonds of this water molecule in turn form O—H⋯Cl hydrogen bonds to two bridging chloride ions on a neighboring polymeric chain. Through the intermediary of the intervening water molecules, each chain thus acts as a hydrogen bond donor towards the neighbouring chains in the [011] and [01$\bar{1}$] directions and as a hydrogen bond acceptor towards the neighbouring chains in the [0$\bar{1}$1] and [0$\bar{1}\bar{1}$] directions (*cf.* Figure 2). It is the lack of centrosymmetry in the hydrogen bonding pattern that accounts for the non-centrosymmetric crystal structure and space group.

   The arsenic atom, the pyridinium ring and the oxygen atom of the water molecule all lie in the same mirror plane (Wyckoff position 2 b). The displacement ellipsoids on the pyridinium ring suggest a slight disorder about this mirror plane, but refining this disorder did not improve the quality of the structural model significantly. The bridging chlorine atom (Cl2) lies on a twofold axis (Wyckoff position 2a).

S2. Experimental

The synthesis reported by Binz & von Schickh (1936) was slightly modified as follows: 3-aminopyridine (20 mmol, 1.882 g) was dissolved in conc. HCl (32%, 15 ml) and As_2O_3 (20 mmol, 3.957 g) and CuCl (2 mmol, 0.198 g) were added to the solution. The solution was cooled in an ice bath to -5 °C. $NaNO_2$ (30 mmol, 2.07 g) was dissolved in water (3 ml) and slowly added to the solution while keeping the temperature below 0 °C. The reaction mixture was then stirred at 35 °C for 8 h. After cooling to r.t. the precipitate was filtered off and washed with 1-molar HCl solution (2 × 20 ml). The filtrate was cooled to -20 °C and after 7 days the product was obtained in the form of large colourless needles.

S3. Refinement

H atoms on the pyridine aromatic ring were positioned geometrically and refined using a riding model with C—H distances constrained to 0.95 Å and the N—H distance constrained to 0.88 Å. U_{iso} for these hydrogen atoms was constrained to $U_{iso}(H) = 1.2 U_{eq}(C \text{ or } N)$. Restraints were applied to the O1—H1 distance and the H1—O1—H1 angle and U_{iso} was constrained to $U_{iso}(H1) = 1.5 U_{eq}(O1)$. The anisotropic displacement parameters of the atoms in the aromatic ring indicate a slight disorder around the mirror plane, but refining this disorder did not improve the structural model significantly.

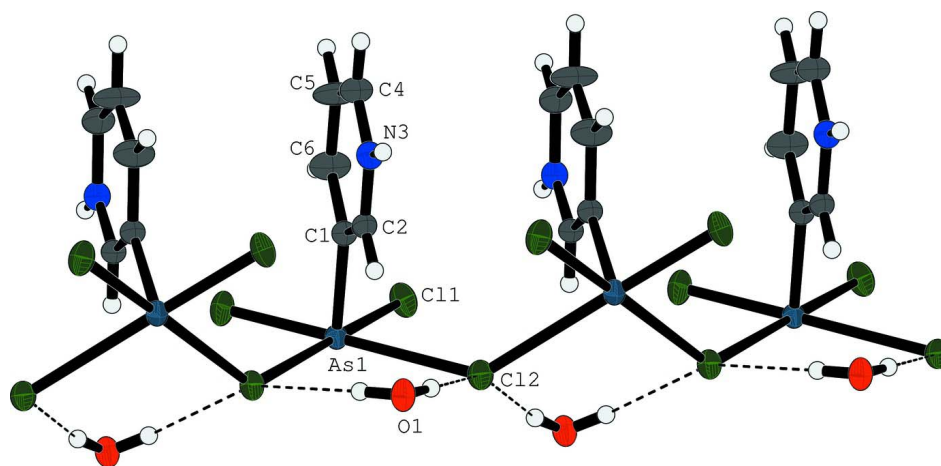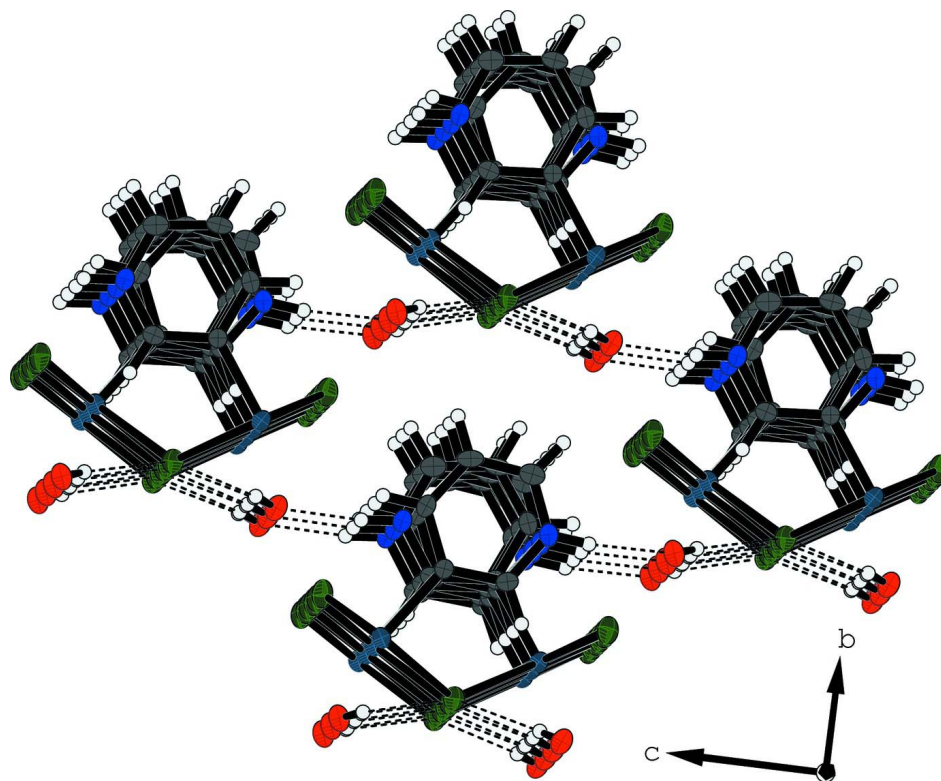**Figure 1**
Polymeric $[C_5H_5NAsCl_3]_\infty$ chain with O—H⋯Cl hydrogen bonds to neighbouring water molecules, showing the labelling scheme in the asymmetric unit. Thermal displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines. Colour code: H white, C grey, N blue, O red, Cl green, As teal.

Figure 2
Four neighbouring chains and their hydrogen bond interactions. Thermal displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines. Colour code: H white, C grey, N blue, O red, Cl green, As teal.

catena-Poly[[[dichlorido(pyridin-1-ium-3-yl)arsenic(III)]-*µ*-chlorido] monohydrate]

Crystal data

[AsCl$_3$(C$_5$H$_5$N)]·H$_2$O
$M_r = 278.39$
Orthorhombic, *Im*2*a*
$a = 8.2107 (9)$ Å
$b = 8.5812 (9)$ Å
$c = 13.2046 (14)$ Å
$V = 930.37 (17)$ Å^3
$Z = 4$
$F(000) = 544$

$D_x = 1.987$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 2911 reflections
$\theta = 2.8–28.2°$
$\mu = 4.46$ mm^{-1}
$T = 200$ K
Block, colourless
$0.5 × 0.2 × 0.2$ mm

Data collection

Bruker SMART APEX CCD
   diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan
   (*SADABS*; Bruker, 1997)
$T_{min} = 0.341$, $T_{max} = 0.469$

3423 measured reflections
1184 independent reflections
1167 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 28.2°$, $\theta_{min} = 2.8°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 9$
$l = -13 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	
$S = 1.10$	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$
1184 reflections	where $P = (F_o^2 + 2F_c^2)/3$
66 parameters	$(\Delta/\sigma)_{max} < 0.001$
3 restraints	$\Delta\rho_{max} = 1.14$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -1.28$ e Å^{-3}
	Absolute structure: Flack (1983), 529 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.006 (12)

Special details

Experimental. R(int) was 0.0767 before and 0.0385 after correction. The Ratio of minimum to maximum transmission is 0.7260. The $\lambda/2$ correction factor is 0.0015.

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
As1	0.7500	0.27357 (4)	0.63175 (3)	0.01702 (14)
Cl1	0.55187 (9)	0.36810 (11)	0.73375 (6)	0.0270 (2)
Cl2	0.5000	0.15046 (13)	0.5000	0.0229 (2)
N3	0.7500	0.5797 (5)	0.3838 (3)	0.0215 (8)
H3	0.7500	0.5690	0.3175	0.026*
C1	0.7500	0.4632 (5)	0.5450 (3)	0.0187 (8)
C2	0.7500	0.4508 (5)	0.4411 (3)	0.0201 (8)
H2	0.7500	0.3509	0.4100	0.024*
C4	0.7500	0.7237 (6)	0.4225 (4)	0.0291 (11)
H4	0.7500	0.8117	0.3788	0.035*
C5	0.7500	0.7435 (6)	0.5249 (4)	0.0402 (14)
H5	0.7500	0.8450	0.5536	0.048*
C6	0.7500	0.6127 (6)	0.5865 (4)	0.0333 (12)
H6	0.7500	0.6250	0.6580	0.040*
O1	0.7500	0.0724 (4)	0.3215 (2)	0.0242 (7)
H1	0.672 (2)	0.093 (6)	0.358 (2)	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0145 (2)	0.0197 (2)	0.0169 (2)	0.000	0.000	0.00251 (18)
Cl1	0.0210 (3)	0.0386 (5)	0.0213 (4)	0.0061 (3)	0.0042 (3)	0.0002 (3)

Cl2	0.0192 (5)	0.0278 (6)	0.0219 (5)	0.000	0.0024 (4)	0.000
N3	0.0224 (19)	0.025 (2)	0.0172 (15)	0.000	0.000	0.0015 (14)
C1	0.0204 (19)	0.018 (2)	0.0173 (19)	0.000	0.000	−0.0001 (16)
C2	0.0194 (19)	0.017 (2)	0.024 (2)	0.000	0.000	−0.0017 (16)
C4	0.034 (3)	0.021 (2)	0.032 (2)	0.000	0.000	0.0019 (18)
C5	0.072 (4)	0.014 (3)	0.034 (3)	0.000	0.000	−0.003 (2)
C6	0.058 (4)	0.025 (3)	0.017 (2)	0.000	0.000	−0.0035 (18)
O1	0.0180 (15)	0.0329 (19)	0.0218 (15)	0.000	0.000	−0.0053 (14)

Geometric parameters (Å, º)

As1—C1	1.990 (4)	C2—H2	0.9500
As1—Cl1	2.2624 (8)	C4—C5	1.363 (7)
As1—Cl2	2.8907 (5)	C4—H4	0.9500
N3—C4	1.337 (7)	C5—C6	1.386 (7)
N3—C2	1.340 (6)	C5—H5	0.9500
N3—H3	0.8800	C6—H6	0.9500
C1—C2	1.377 (6)	O1—H1	0.818 (17)
C1—C6	1.395 (7)		
C1—As1—Cl1	92.83 (9)	N3—C2—C1	119.9 (4)
C1—As1—Cl2	87.28 (9)	N3—C2—H2	120.0
Cl1—As1—Cl1^i	91.95 (4)	C1—C2—H2	120.0
Cl1—As1—Cl2^{ii}	179.25 (3)	N3—C4—C5	119.6 (5)
Cl1—As1—Cl2	88.78 (2)	N3—C4—H4	120.2
Cl2^{ii}—As1—Cl2	90.49 (2)	C5—C4—H4	120.2
As1^{iii}—Cl2—As1	137.13 (5)	C4—C5—C6	118.7 (4)
C4—N3—C2	123.2 (4)	C4—C5—H5	120.6
C4—N3—H3	118.4	C6—C5—H5	120.6
C2—N3—H3	118.4	C5—C6—C1	121.0 (4)
C2—C1—C6	117.5 (4)	C5—C6—H6	119.5
C2—C1—As1	120.7 (3)	C1—C6—H6	119.5
C6—C1—As1	121.8 (3)		
C1—As1—Cl2—As1^{iii}	−26.08 (9)	C6—C1—C2—N3	0.000 (2)
Cl1—As1—Cl2—As1^{iii}	66.82 (2)	As1—C1—C2—N3	180.000 (1)
Cl2^{ii}—As1—Cl2—As1^{iii}	−113.33 (2)	C2—N3—C4—C5	0.000 (2)
Cl1—As1—C1—C2	−133.95 (2)	N3—C4—C5—C6	0.000 (2)
Cl2—As1—C1—C2	−45.308 (11)	C4—C5—C6—C1	0.000 (2)
Cl1—As1—C1—C6	46.05 (2)	C2—C1—C6—C5	0.000 (2)
Cl2—As1—C1—C6	134.692 (12)	As1—C1—C6—C5	180.000 (2)
C4—N3—C2—C1	0.000 (2)		

Symmetry codes: (i) −*x*+3/2, *y*, *z*; (ii) *x*+1/2, *y*, −*z*+1; (iii) −*x*+1, *y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl2	0.82 (2)	2.40 (2)	3.197 (2)	165 (3)

N3—H3···O1^{iv}	0.88	1.84	2.711	173

Symmetry code: (iv) $-x+3/2$, $y+1/2$, $-z+1/2$.