Unusual 4-arsonoanilinium cationic species in the hydrochloride salt of (4-aminophenyl)arsonic acid and formed in the reaction of the acid with copper(II) sulfate, copper(II) chloride and cadmium chloride

Graham Smith and Urs D. Wermuth

Acta Cryst. (2017). **C73**, 325–330

IUCr Journals
CRYSTALLOGRAPHY JOURNALS ONLINE

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see <http://journals.iucr.org/services/authorrights.html>

Unusual 4-arsonoanilinium cationic species in the hydrochloride salt of (4-aminophenyl)arsonic acid and formed in the reaction of the acid with copper(II) sulfate, copper(II) chloride and cadmium chloride

Graham Smith^{a*} and Urs D. Wermuth^b

Received 12 February 2017

Accepted 25 February 2017

Edited by A. R. Kennedy, University of Strathclyde, Scotland

^aScience and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and ^bSchool of Natural Sciences, Griffith University, Nathan, Queensland 4111, Australia. *Correspondence e-mail: gsmith@bigpond.com

Keywords: *p*-arsanilic acid; 4-arsonoanilinium; coordination polymers; copper(II) chloride salts; cadmium chloride salts; hydrogen bonding; crystal structure.

CCDC references: 1534722; 1534721; 1534720; 1534719

Supporting information: this article has supporting information at journals.iucr.org/c

Structures having the unusual protonated 4-arsonoanilinium species, namely in the hydrochloride salt, $\text{C}_6\text{H}_9\text{AsNO}_3^+\cdot\text{Cl}^-$, (I), and the complex salts formed from the reaction of (4-aminophenyl)arsonic acid (*p*-arsanilic acid) with copper(II) sulfate, *i.e.* hexaaquacopper(II) bis(4-arsonoanilinium) disulfate dihydrate, $(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$, (II), with copper(II) chloride, *i.e.* poly[bis(4-arsonoanilinium) [tetra- μ -chlorido-cuprate(II)]], $\{(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{CuCl}_4]\}_n$, (III), and with cadmium chloride, *i.e.* poly[bis(4-arsonoanilinium) [tetra- μ -chlorido-cadmate(II)]], $\{(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{CdCl}_4]\}_n$, (IV), have been determined. In (II), the two 4-arsonoanilinium cations are accompanied by $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cations with sulfate anions. In the isotypic complex salts (III) and (IV), they act as counter-cations to the $\{[\text{CuCl}_4]^{2-}\}_n$ or $\{[\text{CdCl}_4]^{2-}\}_n$ anionic polymer sheets, respectively. In (II), the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion sits on a crystallographic centre of symmetry and displays a slightly distorted octahedral coordination geometry. The asymmetric unit for (II) contains, in addition to half the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion, one 4-arsonoanilinium cation, a sulfate dianion and a solvent water molecule. Extensive $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds link all the species, giving an overall three-dimensional structure. In (III), four of the chloride ligands are related by inversion $[\text{Cu}-\text{Cl} = 2.2826$ (8) and 2.2990 (9) Å], with the other two sites of the tetragonally distorted octahedral CuCl_6 unit occupied by symmetry-generated Cl-atom donors $[\text{Cu}-\text{Cl} = 2.9833$ (9) Å], forming a two-dimensional coordination polymer network substructure lying parallel to (001). In the crystal, the polymer layers are linked across [001] by a number of bridging hydrogen bonds involving $\text{N}-\text{H}\cdots\text{Cl}$ interactions from head-to-head-linked $\text{As}-\text{O}-\text{H}\cdots\text{O}$ 4-arsonoanilinium cations. A three-dimensional network structure is formed. Cd^{II} compound (IV) is isotypic with Cu^{II} complex (III), but with the central CdCl_6 complex repeat unit having a more regular $M-\text{Cl}$ bond-length range $[2.5232$ (12)– 2.6931 (10) Å] compared to that in (III). This series of compounds represents the first reported crystal structures having the protonated 4-arsonoanilinium species.

© 2017 International Union of Crystallography

1. Introduction

The chemistry of (4-aminophenyl)arsonic acid [*p*-arsanilic acid $p\text{-(NH}_2\text{)C}_6\text{H}_4(\text{AsO}_3\text{H}_2)$, PARSH₂] was first described by Ehrlich & Bertheim (1907) and the compound still has veterinary applications as an antihelminth (Steverding, 2010). The crystal structure of this acid has confirmed the presence of an $\text{NH}_3^+-\text{AsO}_2\text{HO}^-$ zwitterion (Shimada, 1961; Nuttall & Hunter, 1996), which has also been found in a number of metal complex structures involving this acid, for example, in the complexes $\{[\text{CdCl}_2(4\text{-NH}_3\text{C}_6\text{H}_4\text{AsO}_3\text{H})]\cdot 2\text{H}_2\text{O}\}_n$ and $[\text{Pb}$

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$\text{C}_6\text{H}_9\text{AsNO}_3^+ \cdot \text{Cl}^-$	$(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	$(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{CuCl}_4]$	$(\text{C}_6\text{H}_9\text{AsNO}_3)_2[\text{CdCl}_4]$
M_r	253.51	835.92	641.47	690.32
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Orthorhombic, $Pbca$
Temperature (K)	200	200	200	200
a, b, c (Å)	16.6534 (8), 7.4129 (3), 7.6073 (4)	15.0784 (6), 11.2302 (4), 8.6756 (4)	7.6315 (4), 7.1244 (4), 38.0925 (15)	7.5525 (4), 7.2578 (3), 38.5872 (17)
α, β, γ (°)	90, 97.795 (4), 90	90, 99.305 (4), 90	90, 90, 90	90, 90, 90
V (Å ³)	930.44 (8)	1449.74 (10)	2071.08 (18)	2115.14 (17)
Z	4	2	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	3.91	3.26	4.77	4.67
Crystal size (mm)	$0.40 \times 0.40 \times 0.15$	$0.30 \times 0.25 \times 0.08$	$0.25 \times 0.25 \times 0.04$	$0.41 \times 0.25 \times 0.10$
Data collection				
Diffractometer	Oxford Diffraction Gemini-S CCD-detector	Oxford Diffraction Gemini-S CCD-detector	Oxford Diffraction Gemini-S CCD-detector	Oxford Diffraction Gemini-S CCD-detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
$T_{\min}, T_{\max}$	0.66, 0.98	0.670, 0.980	0.544, 0.980	0.485, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3922, 1820, 1601	6196, 2846, 2518	6065, 2028, 1715	5452, 2070, 1778
R_{int}	0.026	0.026	0.032	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617	0.617	0.617	0.617
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.068, 1.06	0.027, 0.066, 1.05	0.034, 0.090, 1.13	0.032, 0.070, 1.11
No. of reflections	1820	2846	2028	2070
No. of parameters	124	226	139	139
No. of restraints	5	13	5	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.44, -0.48	0.36, -0.51	0.42, -0.57	0.62, -0.50

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012), and *PLATON* (Spek, 2009).

$(\text{NO}_3)_2(4\text{-NH}_3\text{C}_6\text{H}_4\text{AsO}_3\text{H})]_n$ (Lesikar-Parrish *et al.*, 2013), and less commonly with the monoanionic zwitterionic ligand species, for example, $\{[\text{Zn}_2\text{Cl}_2(4\text{-NH}_3\text{C}_6\text{H}_4\text{AsO}_3)]\text{Cl} \cdot 2\text{H}_2\text{O}\}_n$ (Lesikar-Parrish *et al.*, 2013).

More commonly, the monoanionic nonzwitterionic ligand species hydrogen (4-aminophenyl)arsonate (PARSH^-) is present in metal complexes, although structures of single-metal complexes, *cf.* those with more than one metal, are not very common in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). Examples of mixed-metal polyoxidometallic structures, such as those with Mo/Ag, Mo/Cu, W/Na and V/Na, are known (Breen & Schmitt, 2008; Johnson *et al.*, 2002).

We have previously reported the crystal structures of the hydrogen *p*-arsanilate complex salts with alkali metal complex salts, namely $[\text{Na}(\text{PARSH})(\text{H}_2\text{O})_2]_n$ (Smith & Wermuth, 2014) and the isotypic K, Rb and Cs complexes (Smith & Wermuth, 2017*a*), as well as the structures of the alkaline earth complex salts (Smith & Wermuth, 2017*b*). For the first set, having the general formula $[(M^+)_2 \cdot 2(\text{C}_6\text{H}_6\text{AsNO}_3\text{H}^-) \cdot 3(\text{H}_2\text{O})]_n$, all the species are involved in bonding with the metal ion, with the

PARSH^- anion bonding only through the bridging arsonate O-atom donors, forming two-dimensional layered coordination polymeric substructures. The structure of the NH_4^+ salt (a monohydrate) is also known (Smith & Wermuth, 2014).

Among the alkaline earth set, the Mg complex salt differs from the other members in having the commonly found $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation in a complex salt, with the anionic hydrogen *p*-arsanilate species uncoordinated, the structure being essentially isotypic with the Mn^{2+} salt structure (Smith & Wermuth, 2016). In the other three coordination polymeric structures of the alkaline earth set, the PARSH^- ligands are coordinated and bridging, *viz.* $\{[\text{Ca}(\text{PARSH})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$, (1), $[\text{Sr}(\text{PARSH})_2(\text{H}_2\text{O})_3]_n$, (2), and isotypic $[\text{Ba}(\text{PARSH})_2(\text{H}_2\text{O})_3]_n$, (3).

Although the monoanionic hydrogen *p*-arsanilate species (PARSH^-) is involved in numerous metal coordination environments, it is surprising that examples of the protonated 4-arsonoanilate (PARSH_3^+) species are absent from the CSD. It was considered that in the presence of strong acids, including organic acid analogues, protonation should readily

be achieved. We therefore tried a number of preparations involving PARSH₂ with metal salts under various acidic aqueous conditions and the following compounds were obtained and their structures reported herein: 4-arsonoanilinium chloride, PARSH₃⁺·Cl[−], (I); the double salt hexaaqua-copper(II) bis(4-arsonoanilinium) disulfate dihydrate, (PARSH₃)₂[Cu(H₂O)₆](SO₄)₂·2H₂O, (II); poly[bis(4-arsonoanilinium) [tetra-μ-chlorido-cuprate(II)]]_n, {(PARSH₃)₂[CuCl₄]}_n, (III); and poly[bis(4-arsonoanilinium) [tetra-μ-chlorido-cadmate(II)]]_n, {(PARSH₃)₂[CdCl₄]}_n, (IV).

2. Experimental

2.1. Synthesis and crystallization

Compounds (II) and (III) were synthesized by heating together for 5 min, 1 mmol quantities of (4-aminophenyl)-arsonic acid (PARSH₂) and 0.5 mmol of either CuSO₄·5H₂O or CuCl₂, respectively, in 20 ml of 50% (v/v) ethanol/water. For (IV), a similar procedure to that used for (III) was employed using CdCO₃ with the addition of excess HCl. Room-temperature evaporation of the solutions gave thin pale-blue crystal plates of (II), green crystal plates of (III) and colourless crystal plates of (IV), from which specimens were cleaved for the X-ray analyses. Salt (I) was obtained from the attempted preparation of a cobalt derivative of PARSH₂ using the above procedure with cobalt(II) acetate but with the addition of HCl to achieve dissolution of the initially formed precipitate. Colourless crystal prisms were formed after room-temperature evaporation.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms potentially involved in hydrogen-bonding interactions were located by difference methods but their positional parameters were constrained in the refinement, with N—H = 0.88 (2) Å and O—H = 0.86 (2) Å [or 0.90 (2) Å for (I)], and with *U*_{iso}(H) = 1.2*U*_{eq}(N) or 1.5*U*_{eq}(O). Other H atoms were included in the refinement at calculated positions (C—H = 0.95 Å) and treated as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Figure 1

The molecular configuration and atom-numbering scheme for the 4-arsonoanilinium cation and the chloride anion in the asymmetric unit of (I), with displacement ellipsoids drawn at the 40% probability level and the hydrogen bond shown as a dashed line.

3. Results and discussion

In structures (I)–(IV), the protonated 4-arsonoanilinium cationic species, *i.e.* 4-arsonoanilinium or PARSH₃⁺, is present, namely as a discrete cation in (I), as linker cations between [Cu(H₂O)₆]²⁺ cation and sulfate anion layers in double salt (II), and between polymeric anionic {[CuCl₄]^{2−}]_n layers in (III) or {[CdCl₄]^{2−}]_n layers in the isotypic complex salt (IV). The presence of the cation is confirmed on the basis of chemical stoichiometry, as well as on the basis of chemical stoichiometry, as well as on the basis of the As1—O bond lengths [As1—O11, As1—O13 and As1=O12 are, respectively, 1.688 (3), 1.701 (2) and 1.648 (2) Å for (I); 1.7046 (18), 1.702 (2) and 1.6395 (19) Å for (II); 1.700 (2), 1.706 (3) and 1.644 (2) Å for (III); and 1.697 (3), 1.710 (3) and 1.648 (3) Å for (IV)]. These values compare with the values of 1.737 (6), 1.656 (3) and 1.669 (6) Å in the parent acid zwitterion (Nuttall & Hunter, 1996) and the values of 1.747 (3), 1.672 (3) and 1.677 (2) Å in the monoanionic ligand in the Na complex (Smith & Wermuth, 2014). There are no examples of the cationic PARSH₃⁺ species in the CSD, nor are there any examples of compounds with the analogous protonated (4-aminophenyl)phosphonic acid. We have also found the

Figure 2

The packing in the unit cell of (I), viewed along the *b*-axis, showing the associated cation-linked chloride layers linked peripherally across *a* by hydrogen bonds (dashed lines) involving the 4-arsonoanilinium cations. The symmetry codes are as in Table 2.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O11-H11\cdots O12^i$	0.88 (2)	1.68 (2)	2.563 (3)	178 (5)
$O13-H13\cdots O12^{ii}$	0.87 (3)	1.73 (3)	2.582 (3)	167 (4)
$N4-H41\cdots Cl1^{iii}$	0.87 (2)	2.29 (2)	3.073 (2)	151 (3)
$N4-H42\cdots Cl1$	0.87 (2)	2.27 (2)	3.091 (2)	158 (2)
$N4-H43\cdots Cl1^{iv}$	0.87 (2)	2.30 (2)	3.160 (3)	170 (2)

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

Table 3

Selected bond lengths (Å) for (II).

$Cu1-O3W$	2.013 (2)	$Cu1-O2W$	1.946 (2)
$Cu1-O1W$	2.2702 (18)		

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O11-H11\cdots O3^{ii}$	0.83 (3)	1.76 (3)	2.582 (3)	167 (3)
$O13-H13\cdots O4W$	0.85 (2)	1.79 (2)	2.631 (3)	174 (3)
$O1W-H11W\cdots O4^{iii}$	0.83 (3)	1.92 (3)	2.745 (3)	171 (4)
$O1W-H12W\cdots O2^{ii}$	0.81 (3)	1.90 (3)	2.703 (3)	176 (3)
$O2W-H21W\cdots O4W^{iv}$	0.85 (3)	1.86 (3)	2.698 (3)	170 (3)
$O2W-H22W\cdots O12$	0.83 (3)	1.84 (3)	2.667 (3)	173 (3)
$O3W-H31W\cdots O1^v$	0.82 (2)	2.00 (2)	2.792 (3)	161 (3)
$O3W-H32W\cdots O1^{vi}$	0.84 (2)	1.94 (2)	2.780 (2)	176 (4)
$O4W-H41W\cdots O1W$	0.82 (3)	2.09 (3)	2.858 (3)	157 (3)
$O4W-H42W\cdots O2^{vii}$	0.82 (3)	1.96 (3)	2.753 (3)	164 (3)
$N4-H41\cdots O4^{viii}$	0.89 (3)	1.85 (3)	2.726 (3)	169 (3)
$N4-H42\cdots O3$	0.89 (2)	1.88 (2)	2.767 (3)	175 (2)
$N4-H43\cdots O12^{ix}$	0.90 (2)	1.80 (2)	2.680 (3)	166 (2)
$C2-H2\cdots O11^{iv}$	0.95	2.49	3.385 (3)	157

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

PARSH₃⁺ species in the crystal structures of 1:1 proton-transfer compounds of *p*-arsanilic acid with strong organic acids, for example, picric acid, 3,5-dinitrosalicylic acid, 5-sulfosalicylic acid and *p*-toluenesulfonic acid (Smith & Wermuth, 2017c).

In the crystal structure of (I) (Fig. 1), the PARSH₃⁺ cations are linked through arsonate $O11-H11\cdots O12^i$ and $O13-H13\cdots O12^{ii}$ hydrogen bonds (see Table 2 for details and symmetry codes), generating two-dimensional layered structures lying parallel to (100). The first of these interactions forms centrosymmetric $R_2^2(8)$ ring motifs. In the crystal, the layers are linked across *a* through anilinium $N-H\cdots Cl$ hydrogen bonds (Table 1), giving a three-dimensional structure (Fig. 2). Weak inter-ring $\pi-\pi$ interactions are also present [minimum ring-centroid separation = 2.8304 (16) Å].

In the structure of the Cu^{II} double salt (II) (Fig. 3), the centrosymmetric $[Cu(H_2O)_6]^{2+}$ cation is accompanied by two inversion-related PARSH₃⁺ cations, together with two similarly related sulfate dianions and two water molecules of solvation [O4W and O4Wⁱ; symmetry code: (i) $-x, -y, -z$]. The Cu—OW bond lengths in the slightly tetragonally distorted octahedral coordination polyhedron are 1.946 (2)

Figure 3

The molecular configuration and atom-numbering scheme for the complex cation, the 4-arsonoanilinium cation, the sulfate anion and the water molecule of solvation (O1W) in the asymmetric unit of (II). The Cu²⁺ ion sits on a crystallographic centre of inversion and the asymmetric unit contains half the $[Cu(H_2O)_6]^{2+}$ ion, one 4-arsonoanilinium cation, a sulfate dianion and a solvent water molecule. Non-H atoms are shown as 40% probability displacement ellipsoids. Hydrogen-bonding interactions are shown as dashed lines. [Symmetry code: (i) $-x, -y, -z$.]

and 2.013 (2) (equatorial), and 2.2702 (18) Å (axial) (Table 3). The $[Cu(H_2O)_6]^{2+}$ cation is a very common counter-ion in Cu^{II} complex structures, but no examples involving arsonates and only a few involving analogous phosphonates are known, for example, in a bridged (2-pyridyl *N*-oxide)phosphonate complex (Ma *et al.*, 2007). The amine N group of the PARSH₃⁺ cation is not involved in bonding to the metal atom, unlike that found in a number of *p*-arsanilate complexes, for example, in a second Zn structure (Lin *et al.*, 2012).

In the crystal of (II), the molecular species, including the coordinated water ligands, are involved in O—H $\cdots$ O and N—H $\cdots$ O hydrogen-bonding interactions with arsonate, sulfate and water O-atom acceptors (Table 4). Among these interactions is a cyclic $R_3^3(10)$ motif involving all but the sulfate anion, best seen in Fig. 3. Two-dimensional layered substructures lying parallel to (100) are linked across *a* through PARSH₃⁺ O—H $\cdots$ O and N—H $\cdots$ O hydrogen bonds, giving

Figure 4

The packing in the unit cell of (II), viewed along the *b*-axis direction, showing the associated $[Cu(H_2O)_6]^{2+}$ cation layers linked peripherally across *a* by hydrogen bonds involving the 4-arsonoanilinium cations, the sulfate anions and the water molecules of solvation. Hydrogen-bonding interactions are shown as dashed lines and aromatic H atoms have been omitted. Generic atom labels without symmetry codes have been used.

Table 5
Selected bond lengths (Å) for (III).

Cu1—Cl2 ⁱⁱ	2.9833 (9)	Cu1—Cl2	2.2990 (9)
Cu1—Cl1	2.2826 (8)	Cu1—Cl2 ⁱⁱⁱ	2.9833 (9)

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

Table 6
Selected bond lengths (Å) for (IV).

Cd1—Cl2 ⁱⁱ	2.6931 (10)	Cd1—Cl2	2.6820 (10)
Cd1—Cl1	2.5232 (12)	Cd1—Cl2 ⁱⁱⁱ	2.6931 (10)

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

Table 7
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11...O12 ^{iv}	0.84 (4)	1.78 (4)	2.609 (4)	170 (3)
O13—H13...O12 ^v	0.85 (4)	1.79 (4)	2.610 (4)	162 (4)
N4—H41...Cl1 ⁱⁱ	0.88 (2)	2.38 (2)	3.235 (4)	163 (4)
N4—H42...Cl2 ^{vi}	0.87 (4)	2.47 (4)	3.301 (4)	161 (3)
N4—H43...Cl1	0.89 (3)	2.39 (2)	3.208 (4)	153 (3)
C6—H6...O13 ⁱⁱ	0.95	2.40	3.268 (5)	152

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

an overall three-dimensional supramolecular structure (Fig. 4). No reasonable ring–ring interactions are present [minimum ring-centroid separation = 3.9829 (15) Å].

In the CuCl₆ coordination polyhedron of (III) (Fig. 5), four of the Cl ligands are related by inversion, *i.e.* two monodentate [Cu1—Cl1 and Cu1—Cl1ⁱ = 2.2826 (8) Å; symmetry code: (i) $-x + 1, -y + 1, -z + 1$] and two bridging [Cu1—Cl2 and Cu1—Cl2ⁱ = 2.2990 (9) Å], while two longer axial bonds are from bridging Cl2 donors [Cl2ⁱⁱ and inversion-related Cl2ⁱⁱⁱ, 2.9833 (9) Å; see Table 5 for symmetry codes].

Cd^{II} compound (IV) (Fig. 6) is isotypic with copper(II) complex (III) (Fig. 7) and the basic description of the metal–chloride bonding in the coordination polymeric structure (Tables 5 and 6) and hydrogen bonding (Tables 7 and 8) are essentially the same. The major difference is seen in the Cd—Cl bond lengths in the CdCl₆ coordination polyhedron of the complex repeat unit (Table 6), which are more regular [range 2.5232 (12)–2.6931 (10) Å] compared to those in (III)

Figure 5
The molecular configuration and atom-numbering scheme for the complex unit in (III). The anionic CuCl₆ complex units comprise four inversion-related Cl donors and two Cl donors in the polymer extensions. Non-H atoms are shown as 40% probability displacement ellipsoids. The dashed line represents the N—H...Cl hydrogen bond. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

Table 8
Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11...O12 ^{iv}	0.86 (4)	1.74 (4)	2.597 (4)	175 (3)
O13—H13...O12 ^v	0.88 (4)	1.75 (4)	2.596 (4)	160 (4)
N4—H41...Cl1 ⁱⁱ	0.88 (2)	2.31 (2)	3.178 (4)	170 (5)
N4—H42...Cl2 ^{vi}	0.90 (4)	2.37 (4)	3.257 (4)	168 (3)
N4—H43...Cl1	0.90 (3)	2.30 (2)	3.150 (4)	158 (4)
C6—H6...O13 ⁱⁱ	0.95	2.41	3.246 (5)	146

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

(Table 5). A minor anomaly in the comparison of the two structures is that in the smaller unit cell of (III), the *a* cell parameter [7.6315 (4) Å] is slightly longer than that of (IV) [7.5525 (4) Å] and may be due to the larger axial Cu—Cl2ⁱⁱ and Cu—Cl2ⁱⁱⁱ bond lengths in the tetragonally distorted complex unit.

A two-dimensional coordination polymeric network substructure lying parallel to (001) is generated in both (III) and (IV) through centrosymmetric cyclic eight-membered chloride-bridged units (Fig. 7). In the crystal, the polymer layers are linked across [001] by a number of bridging hydrogen bonds involving N—H...Cl interactions from head-to-head O—H...O-linked 4-arsonoanilinium cations (Tables 7 and 8). An overall three-dimensional network structure is

Figure 6
The molecular configuration and atom-numbering scheme for the complex unit in (IV), with non-H atoms shown as 40% probability displacement ellipsoids. The anionic CdCl₆ complex units have the same symmetry codes as shown for the isotypic Cu²⁺ complex (III) in Fig. 5. The dashed line represents the N—H...Cl hydrogen bond.

Figure 7
The two-dimensional anionic coordination polymeric sheet substructures of (III) and (IV), which lie parallel to (001) in the unit cell, with the 4-arsonoanilinium cations removed. *M* represents Cu²⁺ for (III) and Cd²⁺ for (IV). The PARSH₃⁺ cations have been omitted. (For symmetry codes, see Table 6 and Fig. 5.)

Figure 8

A view of the packing in the unit cells of (III) or (IV), showing the associated cation/anion sheets linked peripherally across *c* by hydrogen bonds (dashed lines) involving the anilinium groups.

formed (Fig. 8). It should also be noted that the Cd^{II} complex reported by Lesikar-Parrish *et al.* (2013), prepared from CdCl_2 using mild aqueous reaction conditions, was $[\text{CdCl}_2(4\text{-NH}_3\text{C}_6\text{H}_4\text{AsO}_3\text{H})(\text{H}_2\text{O})_2]_n$.

The basic *M*–Cl polymeric sheet structures present in both compounds (III) and (IV) are not unusual, with 65 CSD examples present in the case of the less prevalent Cd–Cl structure. However, the eight-membered cyclic unit described for (IV) is not so common, more often being four-membered involving di- μ_2 -chlorido- or tri- μ_2 -chlorido-bridged rings such as are present in the $[\text{CdCl}_4]^{2-}$ complex substructures in complexes with the methylammonium cation (Pabst *et al.*, 1987) and the 2-amino-4,5-dihydro-3*H*-1,3-triazolium cation (Kubiak *et al.*, 1983).

The series of structures reported here represent examples having a previously structurally unreported protonated (4-aminophenyl)arsonic acid, the 4-arsonoanilinium cation. These compounds are various, ranging from a simple hydrochloride to a Cu^{II} double sulfate salt from reaction with aqueous CuSO_4 to counter-cations from the reaction with CuCl_2 or CdCl_2 in the presence of HCl.

Acknowledgements

The authors acknowledge support from the Science and Engineering Faculty, Queensland University of Technology and Griffith University.

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Breen, J. M. & Schmitt, W. (2008). *Angew. Chem. Int. Ed.* **47**, 6904–6908.
- Ehrlich, P. & Berthelm, A. (1907). *Ber. Dtsch. Chem. Ges.* **40**, 3292–3297.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.
- Johnson, B. J. S., Schroden, R. C., Zhu, C., Young, V. G. & Stein, A. (2002). *Inorg. Chem.* **41**, 2213–2218.
- Kubiak, M., Glowiak, T. & Kozłowski, H. (1983). *Acta Cryst. C* **39**, 1637–1639.
- Lesikar-Parrish, L. A., Neilson, R. H. & Richards, A. F. (2013). *J. Solid State Chem.* **198**, 424–432.
- Lin, W.-Z., Liu, Z.-Q., Huang, X.-H., Li, H.-H., Wu, S.-T. & Huang, C.-C. (2012). *Chin. J. Struct. Chem.* **31**, 1301–1308.
- Ma, Y.-S., Wang, T.-W., Li, Y.-Z. & Zheng, L.-M. (2007). *Inorg. Chim. Acta*, **360**, 4117–4124.
- Nuttall, R. H. & Hunter, W. N. (1996). *Acta Cryst. C* **52**, 1681–1683.
- Pabst, I., Fuess, H. & Bats, J. W. (1987). *Acta Cryst. C* **43**, 413–416.
- Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Shimada, A. (1961). *Bull. Chem. Soc. Jpn.* **34**, 639–643.
- Smith, G. & Wermuth, U. D. (2014). *Acta Cryst. C* **70**, 738–741.
- Smith, G. & Wermuth, U. D. (2016). *IUCrData*, **1**, x161985.
- Smith, G. & Wermuth, U. D. (2017a). *Acta Cryst. E* **73**, 203–208.
- Smith, G. & Wermuth, U. D. (2017b). *Acta Cryst. C* **73**, 61–67.
- Smith, G. & Wermuth, U. D. (2017c). Unpublished results.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
- Steveding, D. (2010). *Parasites Vectors*, **3**, 15.

supporting information

Acta Cryst. (2017). **C73**, 325–330 [https://doi.org/10.1107/S205322961700314X]

Unusual 4-arsonoanilinium cationic species in the hydrochloride salt of (4-aminophenyl)arsonic acid and formed in the reaction of the acid with copper(II) sulfate, copper(II) chloride and cadmium chloride

Graham Smith and Urs D. Wermuth

Computing details

For all compounds, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015). Program(s) used to solve structure: *SIR 92* (Altomare *et al.*, 1993) for (I); *SHELXS97* (Sheldrick, 2008) for (II), (III); *SIR92* (Altomare *et al.*, 1993) for (IV). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

(I) 4-Arsonoanilinium chloride

Crystal data

$\text{C}_6\text{H}_9\text{AsNO}_3^+\text{Cl}^-$

$M_r = 253.51$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 16.6534$ (8) Å

$b = 7.4129$ (3) Å

$c = 7.6073$ (4) Å

$\beta = 97.795$ (4)°

$V = 930.44$ (8) Å³

$Z = 4$

$F(000) = 504$

$D_x = 1.810$ Mg m⁻³

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

Cell parameters from 1528 reflections

$\theta = 4.4\text{--}29.2^\circ$

$\mu = 3.91$ mm⁻¹

$T = 200$ K

Plate, colourless

$0.40 \times 0.40 \times 0.15$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.66$, $T_{\max} = 0.98$

3922 measured reflections

1820 independent reflections

1601 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -20 \rightarrow 9$

$k = -8 \rightarrow 9$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.068$

$S = 1.06$

1820 reflections

124 parameters

5 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.3689P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\sigma(F^2)$ 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 ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.37111 (2)	0.53013 (4)	0.52946 (4)	0.0235 (1)
O11	0.43235 (13)	0.4083 (3)	0.6799 (3)	0.0387 (8)
O12	0.41875 (13)	0.6107 (3)	0.3702 (3)	0.0345 (7)
O13	0.32856 (15)	0.6985 (3)	0.6375 (3)	0.0454 (8)
N4	0.08067 (16)	0.0693 (3)	0.2459 (3)	0.0218 (8)
C1	0.28113 (17)	0.3841 (4)	0.4442 (3)	0.0200 (8)
C2	0.28676 (18)	0.1973 (4)	0.4548 (4)	0.0263 (9)
C3	0.22080 (19)	0.0936 (4)	0.3897 (4)	0.0252 (9)
C4	0.15124 (17)	0.1775 (3)	0.3126 (3)	0.0178 (8)
C5	0.14488 (18)	0.3635 (3)	0.2991 (4)	0.0225 (8)
C6	0.21088 (18)	0.4666 (4)	0.3665 (4)	0.0246 (9)
Cl1	0.05319 (5)	-0.22825 (9)	0.51606 (9)	0.0245 (2)
H2	0.33570	0.14160	0.50660	0.0310*
H3	0.22330	-0.03420	0.39800	0.0300*
H5	0.09630	0.41860	0.24480	0.0270*
H6	0.20800	0.59440	0.35950	0.0300*
H11	0.4836 (13)	0.400 (5)	0.664 (5)	0.0580*
H13	0.363 (2)	0.748 (5)	0.720 (4)	0.0680*
H41	0.090 (2)	-0.014 (3)	0.171 (3)	0.0260*
H42	0.0631 (19)	0.008 (3)	0.330 (3)	0.0260*
H43	0.0432 (15)	0.135 (3)	0.185 (3)	0.0260*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0114 (2)	0.0300 (2)	0.0279 (2)	-0.0011 (1)	-0.0019 (1)	-0.0005 (1)
O11	0.0152 (12)	0.0649 (15)	0.0346 (12)	0.0039 (11)	-0.0017 (10)	0.0195 (11)
O12	0.0170 (12)	0.0419 (12)	0.0441 (13)	0.0039 (10)	0.0024 (10)	0.0197 (11)
O13	0.0187 (13)	0.0528 (15)	0.0621 (16)	-0.0012 (11)	-0.0035 (11)	-0.0324 (13)
N4	0.0249 (15)	0.0208 (13)	0.0189 (12)	-0.0069 (11)	0.0001 (10)	0.0011 (10)
C1	0.0163 (15)	0.0247 (14)	0.0188 (13)	-0.0008 (12)	0.0015 (11)	-0.0004 (12)

C2	0.0206 (17)	0.0280 (15)	0.0297 (15)	0.0080 (12)	0.0016 (13)	0.0041 (13)
C3	0.0295 (18)	0.0159 (13)	0.0300 (15)	0.0026 (12)	0.0037 (13)	0.0018 (12)
C4	0.0200 (15)	0.0188 (13)	0.0146 (12)	−0.0040 (11)	0.0027 (11)	−0.0026 (11)
C5	0.0180 (15)	0.0214 (14)	0.0261 (14)	0.0030 (12)	−0.0039 (12)	0.0027 (12)
C6	0.0186 (16)	0.0177 (13)	0.0363 (16)	−0.0016 (12)	−0.0005 (13)	−0.0016 (12)
C11	0.0315 (4)	0.0200 (3)	0.0212 (3)	0.0009 (3)	0.0009 (3)	0.0032 (3)

Geometric parameters (Å, °)

As1—O11	1.688 (2)	C1—C2	1.390 (4)
As1—O12	1.648 (2)	C1—C6	1.380 (4)
As1—O13	1.701 (2)	C2—C3	1.377 (4)
As1—C1	1.891 (3)	C3—C4	1.374 (4)
O11—H11	0.88 (2)	C4—C5	1.386 (3)
O13—H13	0.87 (3)	C5—C6	1.379 (4)
N4—C4	1.456 (4)	C2—H2	0.9500
N4—H41	0.87 (2)	C3—H3	0.9500
N4—H42	0.87 (2)	C5—H5	0.9500
N4—H43	0.87 (2)	C6—H6	0.9500
O11—As1—O12	112.68 (11)	C2—C1—C6	120.9 (3)
O11—As1—O13	108.54 (11)	C1—C2—C3	119.4 (3)
O11—As1—C1	107.71 (11)	C2—C3—C4	119.1 (3)
O12—As1—O13	111.29 (11)	N4—C4—C3	119.6 (2)
O12—As1—C1	113.18 (11)	N4—C4—C5	118.2 (2)
O13—As1—C1	102.89 (12)	C3—C4—C5	122.2 (3)
As1—O11—H11	117 (2)	C4—C5—C6	118.4 (3)
As1—O13—H13	112 (2)	C1—C6—C5	120.0 (3)
H42—N4—H43	113 (3)	C1—C2—H2	120.00
H41—N4—H42	103 (2)	C3—C2—H2	120.00
H41—N4—H43	103 (2)	C2—C3—H3	120.00
C4—N4—H41	114 (2)	C4—C3—H3	120.00
C4—N4—H42	111.6 (18)	C4—C5—H5	121.00
C4—N4—H43	111.3 (15)	C6—C5—H5	121.00
As1—C1—C2	120.4 (2)	C1—C6—H6	120.00
As1—C1—C6	118.7 (2)	C5—C6—H6	120.00
O11—As1—C1—C2	−22.9 (2)	As1—C1—C6—C5	178.4 (2)
O11—As1—C1—C6	159.1 (2)	C2—C1—C6—C5	0.4 (4)
O12—As1—C1—C2	102.3 (2)	C1—C2—C3—C4	1.2 (4)
O12—As1—C1—C6	−75.7 (2)	C2—C3—C4—N4	−179.0 (3)
O13—As1—C1—C2	−137.5 (2)	C2—C3—C4—C5	−0.5 (4)
O13—As1—C1—C6	44.5 (2)	N4—C4—C5—C6	178.3 (3)
As1—C1—C2—C3	−179.1 (2)	C3—C4—C5—C6	−0.3 (4)
C6—C1—C2—C3	−1.2 (4)	C4—C5—C6—C1	0.3 (4)

Hydrogen-bond geometry (Å, °)

<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>
O11—H11 $\cdots$ O12 ⁱ	0.88 (2)	1.68 (2)	2.563 (3)	178 (5)
O13—H13 $\cdots$ O12 ⁱⁱ	0.87 (3)	1.73 (3)	2.582 (3)	167 (4)
N4—H41 $\cdots$ Cl1 ⁱⁱⁱ	0.87 (2)	2.29 (2)	3.073 (2)	151 (3)
N4—H42 $\cdots$ Cl1	0.87 (2)	2.27 (2)	3.091 (2)	158 (2)
N4—H43 $\cdots$ Cl1 ^{iv}	0.87 (2)	2.30 (2)	3.160 (3)	170 (2)

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

(II) Hexaaquacopper(II) bis(4-arsonoanilinium) disulfate dihydrate*Crystal data*

(C₆H₉AsNO₃)₂[Cu(H₂O)₆](SO₄)₂·2H₂O

M_r = 835.92

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 15.0784 (6) Å

b = 11.2302 (4) Å

c = 8.6756 (4) Å

β = 99.305 (4)°

V = 1449.74 (10) Å³

Z = 2

F(000) = 846

D_x = 1.915 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 2421 reflections

θ = 3.8–29.0°

μ = 3.26 mm⁻¹

T = 200 K

Plate, colourless

0.30 × 0.25 × 0.08 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2015)

T_{min} = 0.670, *T_{max}* = 0.980

6196 measured reflections

2846 independent reflections

2518 reflections with *I* > 2σ(*I*)

R_{int} = 0.026

$\theta_{\max}$ = 26.0°, $\theta_{\min}$ = 3.3°

h = -18→17

k = -13→12

l = -9→10

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.027

wR (*F*²) = 0.066

S = 1.05

2846 reflections

226 parameters

13 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0274*P*)² + 0.3694*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.36 e Å⁻³

Δρ_{min} = -0.51 e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\sigma(F^2)$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.33980 (2)	0.10571 (2)	0.24157 (3)	0.0172 (1)
O11	0.36399 (14)	0.0443 (2)	0.4232 (2)	0.0276 (7)
O12	0.26786 (13)	0.02573 (18)	0.1225 (2)	0.0249 (6)
O13	0.30451 (14)	0.24789 (18)	0.2623 (3)	0.0305 (7)
N4	0.71564 (17)	0.1526 (2)	0.0761 (3)	0.0174 (7)
C1	0.45558 (19)	0.1223 (2)	0.1863 (3)	0.0165 (8)
C2	0.4777 (2)	0.2222 (2)	0.1063 (3)	0.0205 (8)
C3	0.5634 (2)	0.2323 (2)	0.0701 (3)	0.0213 (9)
C4	0.62545 (18)	0.1425 (2)	0.1130 (3)	0.0158 (8)
C5	0.6026 (2)	0.0410 (2)	0.1881 (3)	0.0218 (9)
C6	0.5178 (2)	0.0313 (3)	0.2253 (3)	0.0222 (9)
Cu1	0.00000	0.00000	0.00000	0.0135 (1)
O1W	0.01471 (14)	0.10426 (18)	0.2269 (2)	0.0210 (6)
O2W	0.10719 (14)	0.0857 (2)	−0.0346 (2)	0.0246 (7)
O3W	−0.07864 (16)	0.13263 (18)	−0.1006 (2)	0.0251 (7)
S1	0.83825 (5)	0.41681 (6)	−0.01779 (7)	0.0152 (2)
O1	0.89949 (14)	0.33415 (17)	0.0779 (2)	0.0255 (7)
O2	0.85590 (14)	0.53998 (16)	0.0346 (2)	0.0229 (6)
O3	0.74402 (14)	0.38634 (16)	−0.0044 (2)	0.0222 (6)
O4	0.84847 (14)	0.40444 (18)	−0.1831 (2)	0.0232 (6)
O4W	0.13231 (15)	0.30042 (17)	0.2021 (2)	0.0217 (7)
H2	0.43450	0.28290	0.07660	0.0250*
H3	0.57970	0.30060	0.01620	0.0260*
H5	0.64520	−0.02130	0.21360	0.0260*
H6	0.50160	−0.03770	0.27770	0.0270*
H11	0.3229 (18)	0.001 (2)	0.445 (4)	0.0330*
H13	0.2483 (13)	0.260 (3)	0.246 (4)	0.0330*
H41	0.7543 (18)	0.137 (3)	0.163 (3)	0.0270*
H42	0.724 (2)	0.2267 (18)	0.044 (3)	0.0270*
H43	0.720 (2)	0.102 (2)	−0.002 (3)	0.0270*
H11W	−0.0329 (16)	0.105 (3)	0.263 (4)	0.0330*
H12W	0.0537 (19)	0.082 (3)	0.296 (3)	0.0330*
H21W	0.110 (2)	0.116 (3)	−0.123 (3)	0.0330*
H22W	0.155 (2)	0.063 (3)	0.018 (3)	0.0330*
H31W	−0.073 (2)	0.195 (2)	−0.050 (3)	0.0330*
H32W	−0.084 (2)	0.146 (3)	−0.197 (2)	0.0330*
H41W	0.0939 (18)	0.249 (2)	0.182 (4)	0.0330*
H42W	0.126 (2)	0.343 (3)	0.125 (3)	0.0330*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0116 (2)	0.0185 (2)	0.0209 (2)	−0.0023 (1)	0.0008 (1)	−0.0012 (1)
O11	0.0194 (12)	0.0386 (13)	0.0240 (11)	−0.0124 (10)	0.0014 (9)	0.0042 (10)
O12	0.0132 (11)	0.0298 (11)	0.0300 (11)	−0.0017 (9)	−0.0012 (9)	−0.0078 (9)
O13	0.0149 (11)	0.0217 (11)	0.0546 (15)	0.0006 (10)	0.0050 (11)	−0.0056 (10)
N4	0.0141 (13)	0.0190 (12)	0.0186 (12)	0.0008 (11)	0.0010 (10)	0.0005 (10)
C1	0.0126 (14)	0.0174 (14)	0.0185 (14)	−0.0032 (11)	−0.0009 (12)	−0.0011 (11)
C2	0.0153 (15)	0.0178 (14)	0.0275 (15)	0.0040 (12)	0.0012 (12)	0.0040 (12)
C3	0.0205 (16)	0.0170 (14)	0.0259 (15)	−0.0008 (12)	0.0021 (13)	0.0075 (12)
C4	0.0115 (14)	0.0209 (14)	0.0138 (13)	−0.0037 (12)	−0.0016 (11)	−0.0017 (11)
C5	0.0172 (16)	0.0189 (14)	0.0282 (16)	0.0049 (12)	0.0003 (13)	0.0061 (12)
C6	0.0212 (17)	0.0186 (14)	0.0261 (16)	−0.0037 (12)	0.0021 (13)	0.0057 (12)
Cu1	0.0118 (2)	0.0143 (2)	0.0142 (2)	0.0003 (2)	0.0012 (2)	0.0011 (2)
O1W	0.0153 (11)	0.0313 (12)	0.0162 (10)	0.0020 (10)	0.0017 (8)	0.0031 (9)
O2W	0.0157 (11)	0.0363 (13)	0.0212 (11)	−0.0046 (10)	0.0013 (9)	0.0084 (9)
O3W	0.0355 (14)	0.0204 (11)	0.0165 (10)	0.0043 (10)	−0.0043 (10)	−0.0003 (9)
S1	0.0142 (4)	0.0175 (3)	0.0140 (3)	−0.0002 (3)	0.0022 (3)	−0.0002 (3)
O1	0.0300 (13)	0.0258 (11)	0.0191 (10)	0.0114 (10)	−0.0010 (9)	0.0011 (9)
O2	0.0261 (12)	0.0175 (10)	0.0227 (10)	−0.0056 (9)	−0.0028 (9)	−0.0019 (8)
O3	0.0172 (11)	0.0192 (10)	0.0321 (12)	−0.0013 (9)	0.0099 (9)	−0.0017 (8)
O4	0.0169 (11)	0.0391 (12)	0.0138 (10)	−0.0023 (9)	0.0027 (8)	−0.0027 (8)
O4W	0.0212 (12)	0.0193 (11)	0.0239 (11)	−0.0019 (9)	0.0012 (9)	−0.0001 (9)

Geometric parameters ($\text{\AA}$, $^\circ$)

Cu1—O3W	2.013 (2)	O2W—H21W	0.85 (3)
Cu1—O1W	2.2702 (18)	O3W—H31W	0.82 (2)
Cu1—O2W	1.946 (2)	O3W—H32W	0.841 (18)
Cu1—O3W ⁱ	2.013 (2)	O4W—H42W	0.82 (3)
Cu1—O1W ⁱ	2.2702 (18)	O4W—H41W	0.82 (3)
Cu1—O2W ⁱ	1.946 (2)	N4—C4	1.451 (4)
As1—O11	1.7046 (18)	N4—H42	0.89 (2)
As1—O12	1.6395 (19)	N4—H43	0.90 (2)
As1—O13	1.702 (2)	N4—H41	0.89 (3)
As1—C1	1.893 (3)	C1—C2	1.388 (3)
S1—O4	1.4736 (19)	C1—C6	1.392 (4)
S1—O2	1.4668 (19)	C2—C3	1.383 (4)
S1—O3	1.484 (2)	C3—C4	1.385 (4)
S1—O1	1.468 (2)	C4—C5	1.384 (3)
O11—H11	0.83 (3)	C5—C6	1.373 (4)
O13—H13	0.85 (2)	C2—H2	0.9500
O1W—H12W	0.81 (3)	C3—H3	0.9500
O1W—H11W	0.83 (3)	C5—H5	0.9500
O2W—H22W	0.83 (3)	C6—H6	0.9500
O11—As1—O12	112.44 (10)	H31W—O3W—H32W	111 (3)

O11—As1—O13	107.80 (11)	Cu1—O3W—H32W	121 (2)
O11—As1—C1	101.87 (11)	Cu1—O3W—H31W	113.3 (19)
O12—As1—O13	113.22 (11)	H41W—O4W—H42W	105 (3)
O12—As1—C1	115.95 (10)	H42—N4—H43	109 (2)
O13—As1—C1	104.56 (10)	H41—N4—H42	110 (3)
O2W—Cu1—O3W	90.74 (9)	H41—N4—H43	113 (3)
O1W ⁱ —Cu1—O2W	95.08 (8)	C4—N4—H41	107.8 (17)
O2W—Cu1—O2W ⁱ	180.00	C4—N4—H42	109.0 (19)
O2W—Cu1—O3W ⁱ	89.26 (9)	C4—N4—H43	107.7 (19)
O1W ⁱ —Cu1—O3W	92.15 (7)	As1—C1—C2	120.8 (2)
O3W—Cu1—O3W ⁱ	180.00	As1—C1—C6	118.6 (2)
O1W—Cu1—O1W ⁱ	180.00	C2—C1—C6	120.5 (3)
O1W—Cu1—O2W	84.92 (8)	C1—C2—C3	119.3 (2)
O1W—Cu1—O3W	87.85 (7)	C2—C3—C4	119.7 (2)
O3—S1—O4	107.85 (11)	N4—C4—C3	120.0 (2)
O2—S1—O4	110.38 (11)	N4—C4—C5	118.8 (2)
O1—S1—O3	109.42 (11)	C3—C4—C5	121.2 (3)
O1—S1—O4	109.60 (12)	C4—C5—C6	119.2 (3)
O1—S1—O2	110.79 (11)	C1—C6—C5	120.1 (3)
O2—S1—O3	108.74 (12)	C1—C2—H2	120.00
As1—O11—H11	113 (2)	C3—C2—H2	120.00
As1—O13—H13	117 (2)	C2—C3—H3	120.00
H11W—O1W—H12W	107 (3)	C4—C3—H3	120.00
Cu1—O1W—H12W	116 (2)	C4—C5—H5	120.00
Cu1—O1W—H11W	111 (2)	C6—C5—H5	120.00
H21W—O2W—H22W	117 (3)	C1—C6—H6	120.00
Cu1—O2W—H22W	116 (2)	C5—C6—H6	120.00
Cu1—O2W—H21W	120 (2)		
O11—As1—C1—C2	−140.8 (2)	As1—C1—C6—C5	−179.4 (2)
O11—As1—C1—C6	40.3 (2)	C2—C1—C6—C5	1.6 (4)
O12—As1—C1—C2	96.8 (2)	C1—C2—C3—C4	0.5 (4)
O12—As1—C1—C6	−82.2 (2)	C2—C3—C4—N4	−179.7 (2)
O13—As1—C1—C2	−28.6 (2)	C2—C3—C4—C5	1.7 (4)
O13—As1—C1—C6	152.4 (2)	N4—C4—C5—C6	179.2 (2)
As1—C1—C2—C3	178.93 (19)	C3—C4—C5—C6	−2.3 (4)
C6—C1—C2—C3	−2.1 (4)	C4—C5—C6—C1	0.6 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H11 $\cdots$ O3 ⁱⁱ	0.83 (3)	1.76 (3)	2.582 (3)	167 (3)
O13—H13 $\cdots$ O4W	0.85 (2)	1.79 (2)	2.631 (3)	174 (3)
O1W—H11W $\cdots$ O4 ⁱⁱⁱ	0.83 (3)	1.92 (3)	2.745 (3)	171 (4)
O1W—H12W $\cdots$ O2 ⁱⁱ	0.81 (3)	1.90 (3)	2.703 (3)	176 (3)
O2W—H21W $\cdots$ O4W ^{iv}	0.85 (3)	1.86 (3)	2.698 (3)	170 (3)

O2 <i>W</i> —H22 <i>W</i> ···O12	0.83 (3)	1.84 (3)	2.667 (3)	173 (3)
O3 <i>W</i> —H31 <i>W</i> ···O1 ^v	0.82 (2)	2.00 (2)	2.792 (3)	161 (3)
O3 <i>W</i> —H32 <i>W</i> ···O1 ^{vi}	0.84 (2)	1.94 (2)	2.780 (2)	176 (4)
O4 <i>W</i> —H41 <i>W</i> ···O1 <i>W</i>	0.82 (3)	2.09 (3)	2.858 (3)	157 (3)
O4 <i>W</i> —H42 <i>W</i> ···O2 ^{vii}	0.82 (3)	1.96 (3)	2.753 (3)	164 (3)
N4—H41···O4 ^{viii}	0.89 (3)	1.85 (3)	2.726 (3)	169 (3)
N4—H42···O3	0.89 (2)	1.88 (2)	2.767 (3)	175 (2)
N4—H43···O12 ^{ix}	0.90 (2)	1.80 (2)	2.680 (3)	166 (2)
C2—H2···O11 ^{iv}	0.95	2.49	3.385 (3)	157

Symmetry codes: (ii) $-x+1, y-1/2, -z+1/2$; (iii) $x-1, -y+1/2, z+1/2$; (iv) $x, -y+1/2, z-1/2$; (v) $x-1, y, z$; (vi) $x-1, -y+1/2, z-1/2$; (vii) $-x+1, -y+1, -z$; (viii) $x, -y+1/2, z+1/2$; (ix) $-x+1, -y, -z$.

(III) Poly[bis(4-arsonoanilinium) [tetra- μ -chlorido-cuprate(II)]]

Crystal data

(C₆H₉AsNO₃)₂[CuCl₄]

$M_r = 641.47$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 7.6315$ (4) Å

$b = 7.1244$ (4) Å

$c = 38.0925$ (15) Å

$V = 2071.08$ (18) Å³

$Z = 4$

$F(000) = 1260$

$D_x = 2.057$ Mg m⁻³

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

Cell parameters from 1633 reflections

$\theta = 3.9\text{--}29.0^\circ$

$\mu = 4.77$ mm⁻¹

$T = 200$ K

Plate, green

$0.25 \times 0.25 \times 0.04$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.544$, $T_{\max} = 0.980$

6065 measured reflections

2028 independent reflections

1715 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -9 \rightarrow 9$

$k = -3 \rightarrow 8$

$l = -46 \rightarrow 28$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.090$

$S = 1.13$

2028 reflections

139 parameters

5 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.2932P]$

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

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

$\Delta\rho_{\max} = 0.42$ e Å⁻³

$\Delta\rho_{\min} = -0.57$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\sigma(F^2)$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.50000	0.50000	0.50000	0.0224 (2)
Cl1	0.54832 (12)	0.52358 (15)	0.44103 (2)	0.0294 (3)
Cl2	0.70111 (12)	0.73489 (12)	0.50945 (3)	0.0288 (3)
As1	1.05548 (5)	0.75093 (6)	0.29143 (1)	0.0228 (1)
O11	1.2663 (3)	0.8193 (4)	0.28480 (7)	0.0352 (9)
O12	0.9644 (3)	0.6341 (4)	0.25899 (6)	0.0336 (9)
O13	0.9462 (4)	0.9566 (4)	0.29820 (8)	0.0363 (10)
N4	0.9665 (5)	0.4774 (5)	0.44152 (9)	0.0291 (11)
C1	1.0413 (4)	0.6402 (6)	0.33687 (9)	0.0226 (11)
C2	1.1575 (5)	0.6990 (6)	0.36228 (9)	0.0318 (14)
C3	1.1353 (5)	0.6432 (6)	0.39646 (9)	0.0296 (11)
C4	0.9985 (5)	0.5270 (5)	0.40483 (10)	0.0244 (11)
C5	0.8857 (5)	0.4604 (6)	0.37931 (10)	0.0360 (13)
C6	0.9080 (5)	0.5174 (6)	0.34507 (10)	0.0334 (13)
H2	1.25290	0.77810	0.35610	0.0380*
H3	1.21400	0.68470	0.41410	0.0360*
H5	0.79390	0.37630	0.38530	0.0430*
H6	0.83200	0.47230	0.32720	0.0400*
H11	1.321 (5)	0.750 (5)	0.2708 (11)	0.0530*
H13	0.961 (6)	1.033 (6)	0.2812 (10)	0.0550*
H41	0.985 (5)	0.356 (3)	0.4438 (11)	0.0350*
H42	1.046 (4)	0.530 (6)	0.4545 (10)	0.0350*
H43	0.859 (3)	0.506 (5)	0.4486 (10)	0.0350*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0255 (3)	0.0225 (4)	0.0191 (3)	−0.0066 (3)	0.0005 (3)	0.0006 (3)
Cl1	0.0326 (5)	0.0355 (6)	0.0200 (5)	−0.0028 (4)	0.0018 (4)	0.0006 (4)
Cl2	0.0300 (5)	0.0261 (5)	0.0302 (5)	−0.0094 (4)	−0.0015 (4)	−0.0001 (4)
As1	0.0241 (2)	0.0295 (3)	0.0149 (2)	0.0019 (2)	0.0007 (1)	0.0009 (2)
O11	0.0292 (15)	0.0446 (19)	0.0319 (15)	−0.0032 (14)	0.0086 (12)	−0.0056 (14)
O12	0.0379 (15)	0.0431 (19)	0.0198 (14)	−0.0001 (13)	−0.0064 (11)	−0.0016 (13)
O13	0.0402 (16)	0.0367 (19)	0.0321 (15)	0.0121 (13)	0.0116 (13)	0.0076 (14)
N4	0.0339 (18)	0.033 (2)	0.0204 (17)	0.0044 (16)	0.0026 (14)	0.0052 (16)
C1	0.0260 (18)	0.024 (2)	0.0177 (18)	0.0011 (15)	−0.0012 (14)	0.0035 (16)
C2	0.033 (2)	0.039 (3)	0.0234 (19)	−0.0129 (18)	−0.0010 (16)	0.0047 (18)
C3	0.033 (2)	0.034 (2)	0.0219 (18)	−0.0086 (18)	−0.0082 (16)	−0.0007 (18)
C4	0.0273 (19)	0.025 (2)	0.0208 (19)	0.0033 (16)	0.0045 (15)	0.0024 (16)
C5	0.036 (2)	0.048 (3)	0.0240 (18)	−0.020 (2)	−0.0017 (18)	0.0030 (19)

C6	0.032 (2)	0.047 (3)	0.0212 (18)	−0.0145 (19)	−0.0070 (17)	−0.0005 (19)
----	-----------	-----------	-------------	--------------	--------------	--------------

Geometric parameters (Å, °)

Cu1—Cl2 ⁱ	2.2990 (9)	N4—H41	0.88 (2)
Cu1—Cl2 ⁱⁱ	2.9833 (9)	N4—H42	0.87 (4)
Cu1—Cl1 ⁱ	2.2826 (8)	N4—H43	0.89 (3)
Cu1—Cl1	2.2826 (8)	C1—C2	1.378 (5)
Cu1—Cl2	2.2990 (9)	C1—C6	1.378 (5)
Cu1—Cl2 ⁱⁱⁱ	2.9833 (9)	C2—C3	1.372 (5)
As1—O12	1.644 (2)	C3—C4	1.370 (5)
As1—O13	1.706 (3)	C4—C5	1.383 (5)
As1—C1	1.905 (4)	C5—C6	1.377 (5)
As1—O11	1.700 (2)	C2—H2	0.9500
O11—H11	0.84 (4)	C3—H3	0.9500
O13—H13	0.85 (4)	C5—H5	0.9500
N4—C4	1.462 (5)	C6—H6	0.9500
O11—As1—C1	107.90 (13)	C4—N4—H42	109 (2)
O11—As1—O12	115.70 (12)	C4—N4—H43	113 (2)
O11—As1—O13	103.83 (14)	As1—C1—C2	118.4 (3)
O13—As1—C1	100.98 (16)	As1—C1—C6	120.7 (3)
O12—As1—O13	109.99 (14)	C2—C1—C6	120.6 (3)
O12—As1—C1	116.69 (15)	C1—C2—C3	119.9 (4)
Cl1—Cu1—Cl2	89.58 (4)	C2—C3—C4	119.4 (4)
Cl2—Cu1—Cl2 ⁱ	180.00	N4—C4—C3	119.7 (3)
Cl2—Cu1—Cl2 ⁱⁱ	86.07 (3)	N4—C4—C5	119.0 (3)
Cl1 ⁱ —Cu1—Cl2 ⁱⁱⁱ	92.40 (3)	C3—C4—C5	121.2 (4)
Cl2 ⁱ —Cu1—Cl2 ⁱⁱ	93.93 (3)	C4—C5—C6	119.2 (4)
Cl1—Cu1—Cl2 ⁱ	90.42 (4)	C1—C6—C5	119.6 (4)
Cl1—Cu1—Cl2 ⁱⁱⁱ	87.60 (3)	C1—C2—H2	120.00
Cl1—Cu1—Cl1 ⁱ	180.00	C3—C2—H2	120.00
Cu1—Cl2—Cu1 ^{iv}	162.25 (5)	C2—C3—H3	120.00
As1—O11—H11	113 (3)	C4—C3—H3	120.00
As1—O13—H13	112 (3)	C4—C5—H5	120.00
H42—N4—H43	112 (3)	C6—C5—H5	120.00
H41—N4—H42	105 (4)	C1—C6—H6	120.00
H41—N4—H43	110 (3)	C5—C6—H6	120.00
C4—N4—H41	108 (3)		
O11—As1—C1—C2	28.1 (4)	As1—C1—C6—C5	−170.7 (3)
O11—As1—C1—C6	−157.8 (3)	C2—C1—C6—C5	3.2 (6)
O12—As1—C1—C2	160.4 (3)	C1—C2—C3—C4	0.9 (6)
O12—As1—C1—C6	−25.6 (4)	C2—C3—C4—N4	−175.7 (4)
O13—As1—C1—C2	−80.4 (3)	C2—C3—C4—C5	2.0 (6)
O13—As1—C1—C6	93.6 (3)	N4—C4—C5—C6	175.5 (4)

As1—C1—C2—C3	170.5 (3)	C3—C4—C5—C6	−2.3 (6)
C6—C1—C2—C3	−3.5 (6)	C4—C5—C6—C1	−0.3 (6)

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

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H11 $\cdots$ O12 ^v	0.84 (4)	1.78 (4)	2.609 (4)	170 (3)
O13—H13 $\cdots$ O12 ^{vi}	0.85 (4)	1.79 (4)	2.610 (4)	162 (4)
N4—H41 $\cdots$ C11 ⁱⁱ	0.88 (2)	2.38 (2)	3.235 (4)	163 (4)
N4—H42 $\cdots$ C12 ^{iv}	0.87 (4)	2.47 (4)	3.301 (4)	161 (3)
N4—H43 $\cdots$ C11	0.89 (3)	2.39 (2)	3.208 (4)	153 (3)
C6—H6 $\cdots$ O13 ⁱⁱ	0.95	2.40	3.268 (5)	152

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

(IV) Poly[bis(4-arsonoanilinium) [tetra- μ -chlorido-cadmate(II)]]

Crystal data

(C₆H₉AsNO₃)₂[CdCl₄]

$M_r = 690.32$

Orthorhombic, *Pbca*

Hall symbol: $-P\ 2ac\ 2ab$

$a = 7.5525\ (4)\ \text{\AA}$

$b = 7.2578\ (3)\ \text{\AA}$

$c = 38.5872\ (17)\ \text{\AA}$

$V = 2115.14\ (17)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1336$

$D_x = 2.168\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1959 reflections

$\theta = 3.9\text{--}28.7^\circ$

$\mu = 4.67\ \text{mm}^{-1}$

$T = 200\ \text{K}$

Plate, colourless

$0.41 \times 0.25 \times 0.10\ \text{mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: ENHANCE (Mo) X-ray
source

Graphite monochromator

Detector resolution: $16.077\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.485$, $T_{\max} = 0.980$

5452 measured reflections

2070 independent reflections

1778 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -9 \rightarrow 6$

$k = -8 \rightarrow 7$

$l = -44 \rightarrow 47$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.070$

$S = 1.11$

2070 reflections

139 parameters

5 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$

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

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

$\Delta\rho_{\max} = 0.62\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.50\ \text{e \AA}^{-3}$

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\sigma(F^2)$ 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 ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.50000	0.50000	0.50000	0.0145 (1)
Cl1	0.55662 (14)	0.52125 (14)	0.43568 (3)	0.0211 (3)
Cl2	0.70634 (14)	0.79615 (13)	0.50986 (3)	0.0194 (3)
As1	1.05703 (6)	0.75535 (6)	0.29043 (1)	0.0155 (1)
O11	1.2690 (4)	0.8254 (4)	0.28422 (7)	0.0237 (10)
O12	0.9688 (4)	0.6397 (4)	0.25798 (7)	0.0222 (9)
O13	0.9450 (4)	0.9568 (4)	0.29732 (8)	0.0251 (10)
N4	0.9693 (5)	0.4583 (5)	0.43687 (9)	0.0203 (11)
C1	1.0425 (6)	0.6420 (6)	0.33478 (9)	0.0161 (11)
C2	1.1509 (6)	0.7069 (6)	0.36094 (10)	0.0227 (14)
C3	1.1299 (6)	0.6438 (6)	0.39430 (10)	0.0213 (12)
C4	1.0021 (5)	0.5170 (5)	0.40065 (10)	0.0160 (12)
C5	0.8963 (6)	0.4450 (6)	0.37506 (11)	0.0253 (16)
C6	0.9169 (6)	0.5087 (6)	0.34161 (10)	0.0233 (14)
H2	1.24010	0.79520	0.35590	0.0270*
H3	1.20330	0.68800	0.41250	0.0260*
H5	0.81070	0.35320	0.38030	0.0310*
H6	0.84530	0.46130	0.32340	0.0280*
H11	1.331 (6)	0.758 (5)	0.2703 (10)	0.0360*
H13	0.952 (6)	1.034 (5)	0.2798 (9)	0.0380*
H41	0.974 (6)	0.337 (3)	0.4383 (12)	0.0240*
H42	1.048 (5)	0.515 (5)	0.4508 (10)	0.0240*
H43	0.858 (3)	0.492 (5)	0.4422 (11)	0.0240*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0138 (2)	0.0150 (2)	0.0146 (2)	−0.0006 (2)	0.0006 (2)	0.0013 (2)
Cl1	0.0220 (6)	0.0257 (6)	0.0155 (5)	0.0001 (4)	0.0018 (4)	−0.0001 (4)
Cl2	0.0191 (5)	0.0182 (5)	0.0210 (5)	−0.0071 (4)	0.0016 (4)	−0.0006 (4)
As1	0.0148 (2)	0.0205 (2)	0.0112 (2)	0.0011 (2)	0.0003 (2)	0.0006 (2)
O11	0.0169 (17)	0.0326 (18)	0.0215 (15)	−0.0013 (14)	0.0061 (13)	−0.0052 (14)
O12	0.0217 (17)	0.0261 (16)	0.0187 (15)	0.0003 (14)	−0.0056 (13)	−0.0027 (13)
O13	0.0287 (19)	0.0232 (17)	0.0233 (16)	0.0094 (14)	0.0066 (15)	0.0043 (13)
N4	0.019 (2)	0.027 (2)	0.0149 (18)	0.0003 (17)	0.0016 (16)	0.0017 (16)
C1	0.020 (2)	0.017 (2)	0.0113 (19)	0.0024 (18)	−0.0014 (17)	0.0020 (16)

C2	0.024 (3)	0.027 (2)	0.017 (2)	−0.011 (2)	−0.0014 (19)	0.0017 (18)
C3	0.025 (2)	0.025 (2)	0.014 (2)	−0.006 (2)	−0.0034 (18)	0.0014 (18)
C4	0.016 (2)	0.015 (2)	0.017 (2)	0.0051 (17)	0.0032 (18)	−0.0002 (16)
C5	0.021 (3)	0.033 (3)	0.022 (2)	−0.014 (2)	0.001 (2)	0.002 (2)
C6	0.021 (2)	0.034 (3)	0.015 (2)	−0.007 (2)	−0.0064 (19)	−0.0040 (19)

Geometric parameters (Å, °)

Cd1—Cl2 ⁱ	2.6820 (10)	N4—H41	0.88 (2)
Cd1—Cl2 ⁱⁱ	2.6931 (10)	N4—H42	0.90 (4)
Cd1—Cl1 ⁱ	2.5232 (12)	N4—H43	0.90 (3)
Cd1—Cl1	2.5232 (12)	C1—C2	1.382 (6)
Cd1—Cl2	2.6820 (10)	C1—C6	1.380 (6)
Cd1—Cl2 ⁱⁱⁱ	2.6931 (10)	C2—C3	1.376 (6)
As1—O11	1.697 (3)	C3—C4	1.356 (6)
As1—O12	1.648 (3)	C4—C5	1.374 (6)
As1—O13	1.710 (3)	C5—C6	1.380 (6)
As1—C1	1.902 (4)	C2—H2	0.9500
O11—H11	0.86 (4)	C3—H3	0.9500
O13—H13	0.88 (4)	C5—H5	0.9500
N4—C4	1.482 (5)	C6—H6	0.9500
Cl1—Cd1—Cl2	89.55 (3)	C4—N4—H41	110 (3)
Cl1—Cd1—Cl2 ⁱⁱⁱ	88.11 (3)	C4—N4—H42	109 (2)
Cl1—Cd1—Cl1 ⁱ	180.00	C4—N4—H43	107 (3)
Cl1—Cd1—Cl2 ⁱ	90.45 (3)	As1—C1—C2	118.4 (3)
Cl1—Cd1—Cl2 ⁱⁱ	91.89 (3)	As1—C1—C6	121.0 (3)
Cl2—Cd1—Cl2 ⁱⁱⁱ	93.34 (3)	C2—C1—C6	120.4 (4)
Cl1 ⁱ —Cd1—Cl2	90.45 (3)	C1—C2—C3	120.1 (4)
Cl2—Cd1—Cl2 ⁱ	180.00	C2—C3—C4	118.5 (4)
Cl2—Cd1—Cl2 ⁱⁱ	86.66 (3)	N4—C4—C3	119.0 (3)
O11—As1—C1	108.13 (17)	N4—C4—C5	118.1 (3)
O11—As1—O12	115.27 (14)	C3—C4—C5	122.9 (4)
O11—As1—O13	103.45 (14)	C4—C5—C6	118.7 (4)
O13—As1—C1	101.62 (17)	C1—C6—C5	119.4 (4)
O12—As1—O13	110.70 (15)	C1—C2—H2	120.00
O12—As1—C1	116.10 (16)	C3—C2—H2	120.00
Cd1—Cl2—Cd1 ^{iv}	154.00 (4)	C2—C3—H3	121.00
As1—O11—H11	115 (3)	C4—C3—H3	121.00
As1—O13—H13	113 (3)	C4—C5—H5	121.00
H42—N4—H43	111 (3)	C6—C5—H5	121.00
H41—N4—H42	113 (4)	C1—C6—H6	120.00
H41—N4—H43	107 (4)	C5—C6—H6	120.00
Cl1—Cd1—Cl2—Cd1 ^{iv}	−45.92 (10)	As1—C1—C6—C5	−172.4 (3)
O11—As1—C1—C2	32.4 (4)	C2—C1—C6—C5	2.2 (7)
O11—As1—C1—C6	−152.9 (3)	C1—C2—C3—C4	0.4 (7)
O12—As1—C1—C2	163.8 (3)	C2—C3—C4—N4	−175.5 (4)

O12—As1—C1—C6	−21.6 (4)	C2—C3—C4—C5	2.0 (6)
O13—As1—C1—C2	−76.1 (4)	N4—C4—C5—C6	175.3 (4)
O13—As1—C1—C6	98.6 (4)	C3—C4—C5—C6	−2.2 (6)
As1—C1—C2—C3	172.3 (3)	C4—C5—C6—C1	0.1 (6)
C6—C1—C2—C3	−2.4 (7)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H11 $\cdots$ O12 ^v	0.86 (4)	1.74 (4)	2.597 (4)	175 (3)
O13—H13 $\cdots$ O12 ^{vi}	0.88 (4)	1.75 (4)	2.596 (4)	160 (4)
N4—H41 $\cdots$ C11 ⁱⁱ	0.88 (2)	2.31 (2)	3.178 (4)	170 (5)
N4—H42 $\cdots$ C12 ^{iv}	0.90 (4)	2.37 (4)	3.257 (4)	168 (3)
N4—H43 $\cdots$ C11	0.90 (3)	2.30 (2)	3.150 (4)	158 (4)
C6—H6 $\cdots$ O13 ⁱⁱ	0.95	2.41	3.246 (5)	146

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