Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structures and hydrogen bonding in the isotypic series of hydrated alkali metal (K, Rb and Cs) complexes with 4-aminophenylarsonic acid

Graham Smith[a]* and Urs D. Wermuth[b]

[a]Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and [b]School of Natural Sciences, Griffith University, Nathan, Queensland 4111, Australia. *Correspondence e-mail: gsmith@bigpond.com

Received 7 December 2016
Accepted 10 January 2017

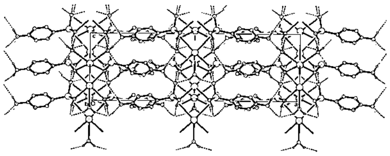
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; *p*-arsanilic acid; coordination polymers; alkali metal salts; hydrogen bonding.

CCDC references: 1526425; 1526424; 1526423

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

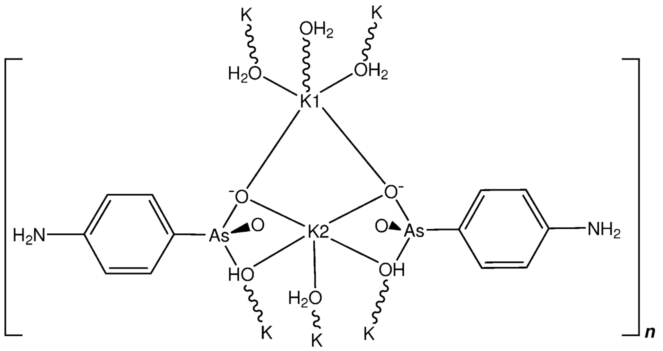
The structures of the alkali metal (K, Rb and Cs) complex salts with 4-aminophenylarsonic acid (*p*-arsanilic acid) manifest an isotypic series with the general formula $[M_2(C_6H_7AsNO_3)_2(H_2O)_3]$, with M = K {poly[di-μ_3-4-aminophenylarsonato-tri-μ_2-aqua-dipotassium], $[K_2(C_6H_7AsNO_3)_2(H_2O)_3]$, (I)}, Rb {poly[di-$\mu_3$-4-aminophenylarsonato-tri-μ_2-aqua-dirubidium], $[Rb_2(C_6H_7AsNO_3)_2(H_2O)_3]$, (II)}, and Cs {poly[di-μ_3-4-aminophenylarsonato-tri-μ_2-aqua-dirubidium], $[Cs_2(C_6H_7AsNO_3)_2(H_2O)_3]$, (III)}, in which the repeating structural units lie across crystallographic mirror planes containing two independent and different metal cations and a bridging water molecule, with the two hydrogen *p*-arsanilate ligands and the second water molecule lying outside the mirror plane. The bonding about the two metal cations in all complexes is similar, one five-coordinate, the other progressing from five-coordinate in (I) to eight-coordinate in both (II) and (III), with overall M—O bond-length ranges of 2.694 (5)–3.009 (7) (K), 2.818 (4)–3.246 (4) (Rb) and 2.961 (9)–3.400 (10) Å (Cs). The additional three bonds in (II) and (III) are the result of inter-metal bridging through the water ligands. Two-dimensional coordination polymeric structures with the layers lying parallel to (100) are generated through a number of bridging bonds involving the water molecules (including hydrogen-bonding interactions), as well as through the arsanilate O atoms. These layers are linked across [100] through amine N—H···O hydrogen bonds to arsonate and water O-atom acceptors, giving overall three-dimensional network structures.



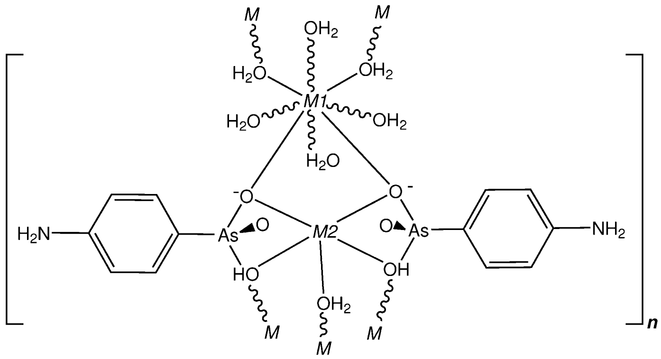
1. Chemical context

Arsenical 4-aminophenylarsonic acid (*p*-arsanilic acid) has biological significance as an anti-helminth in veterinary applications (Steverding, 2010; O'Neil, 2001) and as a hydrated sodium salt (atoxyl) that had early usage as an anti-syphilitic (Ehrlich & Bertheim, 1907; Bosch & Rosich, 2008). The crystal structure of this salt has been determined together with the NH_4^+ salt (Smith & Wermuth, 2014); the structure of the parent *p*-arsanilic acid, which exists as a zwitterion, is also known (Shimada, 1961; Nuttall & Hunter, 1996). We have also determined the structures of the alkaline earth metal (Mg, Ca, Sr, Ba) salts of the acid (Smith & Wermuth, 2017). However, simple *p*-arsanilate single-metal complex structures are not common in the Cambridge Structure Database (Groom *et al.*, 2016), examples being with Ag^I (three forms), Zn, Pb and Cd (Lesikar-Parrish *et al.*, 2013; Xiao *et al.*, 2015); Zn (Lin *et al.*, 2012); Cd (Liu *et al.*, 2010); Sn^{IV} (Xie *et al.*, 2008); V^{IV} and V^V (Breen *et al.*, 2012; Chen *et al.*, 2012; Khan *et al.*, 1992); UO_2 (Adelani *et al.*, 2012). Mixed-metal and/or mixed-ligand complexes are common, *e.g.* $Co^{II}/Mo{=}O$, $Ni^{II}/Mo{=}O$, $Cu^{II}/$

$\text{Mo}{=}\text{O}$ and $\text{Zn/Mo}{=}\text{O}$ with *p*-arsanilate and ligands such as 2,2′-bipyridine, 4,4′-bipyridine and 1,10-phenanthroline (Smith *et al.*, 2013).



(I)



M = Rb (II): *M* = Cs (III):

In an attempt to complete the structures of the alkali metal series of *p*-arsanilate salts, our reaction of the acid with potassium carbonate, rubidium carbonate and caesium carbonate in ethanol/water resulted in the formation of the crystalline hydrated salts with general formula [$M^{+}{}_{2}(C_6H_7AsNO_3)^{-}{}_{2}\cdot 3H_2O$]. Compounds (I) (*M* = K), (II) (Rb) and (III) (Cs) and their crystal structures are reported herein. However, suitable crystals of the Li analogue were not obtained to allow its crystal structure determination.

2. Structural commentary

The structures of the three title compounds [(I), (II) and (III)] form an isotypic series, with the asymmetric units in each comprising two independent and different metal complex cations (*M*1 and *M*2), which lie on crystallographic mirror planes that also contain one of the coordinating water molecules (O2*W*), with the hydrogen *p*-arsanilate ligands and the second water molecules (O*W*1, O1*W*^{ii}) [symmetry code: (ii) $-x + 1, -y, z$] lying across the mirror plane (Figs. 1, 2 and 3, respectively). In all three examples, the *M*2 cation is five-coordinate, while with *M*1, the coordination spheres progress from five-coordinate in (I) to eight-coordinate in (II) and (III). The overall *M*—O bond length ranges are 2.694 (5)–3.009 (7) Å (K) (Table 1), 2.818 (4)–3.246 (4) Å (Rb) (Table 2) and 2.961 (9)–3.400 (10) Å (Cs) (Table 2). The amine N atom is not involved in bonding to the metal, as is the case in a number of other *p*-arsanilate complexes, *e.g.* with Zn (Lin *et al.*, 2012). The *M*1O$_5$ polyhedra in all three structures comprise four bridging arsonate O atoms and the μ_2 bridging water molecule (O2*W*) (Tables 1, 2 and 3). The second *M*2O$_5$ polyhedron in (I) comprises the bridging O11 and O11^{ii}

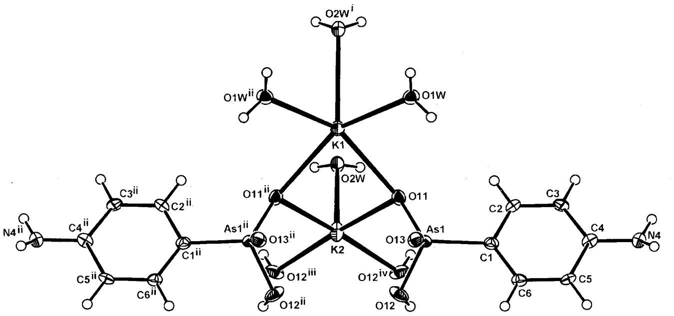


Figure 1

The molecular configuration and atom numbering scheme for the complex unit in (I). The metal cations (K1 and K2) and the water molecule (O2*W*) lie on a mirror plane with mirror-related atoms indicated by symmetry code (ii) $-x + 1, -y, z + \frac{1}{2}$. For other codes, see Table 1. Non-H atoms are shown as displacement ellipsoids at the 40% probability level.

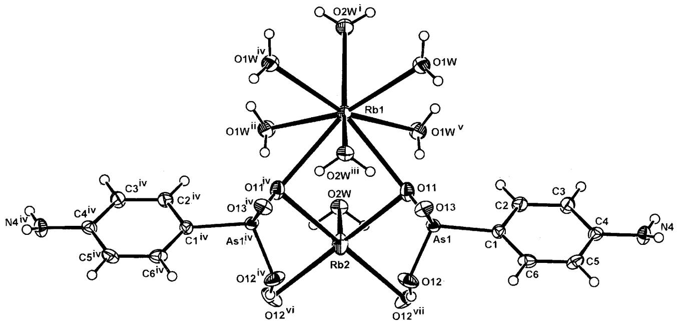


Figure 2

The molecular configuration and atom numbering scheme for the complex unit in the isotypic structure (II). The metal cations (Rb1 and Rb2) and the water molecule (O2*W*) also lie on a mirror plane. For symmetry codes, see Table 2. Non-H atoms are shown as displacement ellipsoids at the 40% probability level.

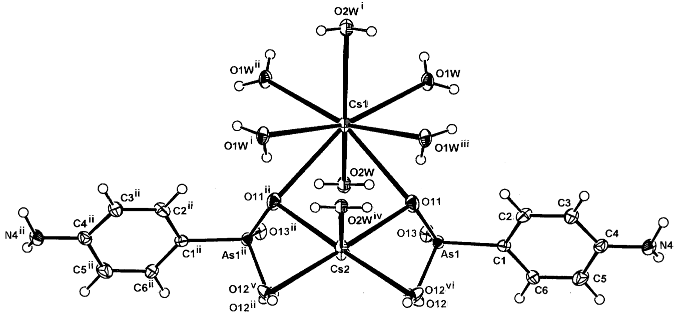


Figure 3

The molecular configuration and atom numbering scheme for the complex unit in the isotypic structure (III). The metal cations (Cs1 and Cs2) and the water molecule (O2*W*) also lie on a mirror plane. For symmetry codes, see Table 3. Non-H atoms are shown as displacement ellipsoids at the 40% probability level.

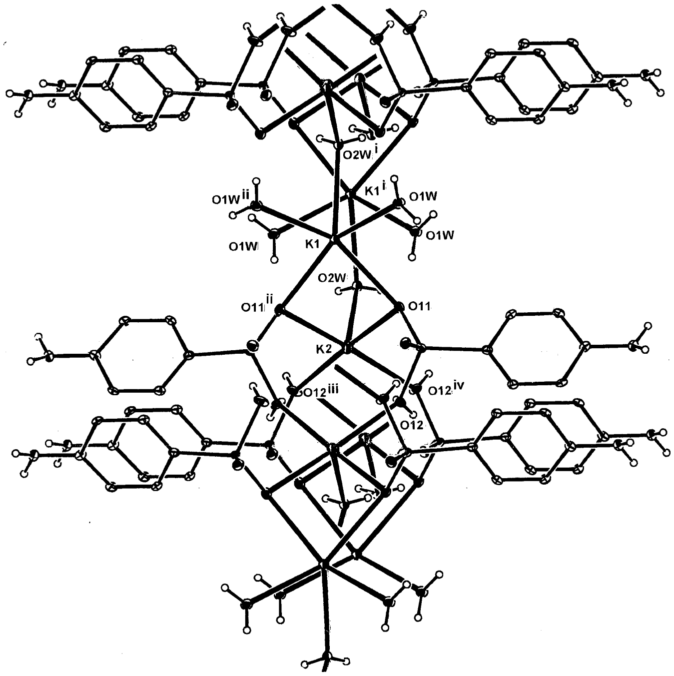


Figure 4
A partial expansion of the two-dimensional coordination polymeric sheet structure of (I), which extends across the mirror plane parallel to (100). Aromatic H atoms are omitted. For symmetry codes, see Table 1.

donors, the μ_2-O2$W^{\rm i}$ [symmetry code: (i) $-x+1, -y+2, z+\frac{1}{2}$] donor and two monodentate water molecules (O1W and O1$W^{\rm i}$) (Table 1).

With (II) and (III), the irregular M2O$_8$ coordination sphere comprises all bonds mentioned in the description of the K complex (I), and in addition, the Rb and Cs bond length expansion allows further coordination sites through additional bridging bonds to both of the water molecules (two through O1W and one through O2W), (Tables 2 and 3). The $M1\cdots M2$ separations are 4.139 (3) Å [for (I)], 4.2500 (11) Å [for (II)] and 4.3498 (15) Å [for (III)]. There are also slightly shorter $M1\cdots M1^{\rm i}$ separations in all structures: 4.079 (3) Å (I), 4.1953 (13) Å (II) and 4.3127 (16) Å (III). Relatively short $M2\cdots$As1 separations are present within the repeat unit in all three structures: 3.6369 (19) Å (I), 3.7796 (8) Å (II) and 3.9488 (14) Å (III).

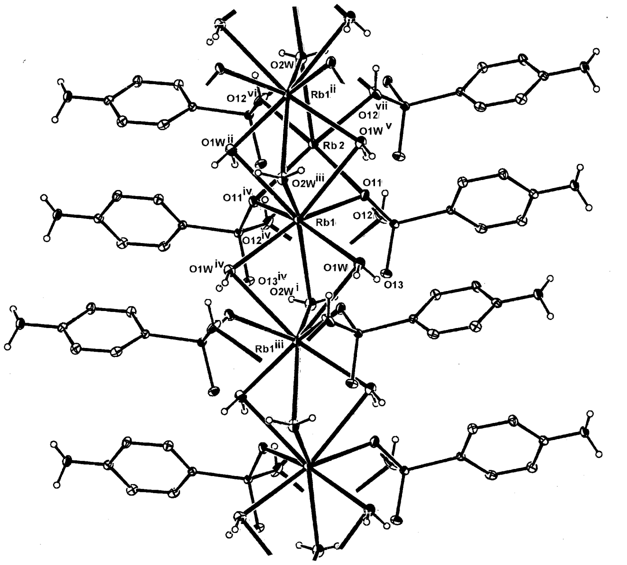


Figure 5
A partial expansion of the two-dimensional coordination polymeric sheet structure of (II) [or (III)], which extends across the mirror plane parallel to (100). Aromatic H atoms have been omitted.

Table 1
Selected bond lengths (Å) for (I).

K1—O1W	2.766 (5)	K2—O2W	3.009 (7)
K1—O11	2.824 (4)	K2—O11	2.713 (5)
K1—O2$W^{\rm i}$	2.959 (7)	K2—O12$^{\rm iii}$	2.694 (5)
K1—O1$W^{\rm ii}$	2.766 (5)	K2—O11$^{\rm ii}$	2.713 (5)
K1—O11$^{\rm ii}$	2.824 (4)	K2—O12$^{\rm iv}$	2.694 (5)

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

Table 2
Selected bond lengths (Å) for (II).

Rb1—O1W	2.917 (4)	Rb1—O1$W^{\rm v}$	3.246 (4)
Rb1—O11	2.925 (3)	Rb2—O2W	3.193 (6)
Rb1—O2$W^{\rm i}$	3.151 (6)	Rb2—O11	2.863 (3)
Rb1—O1$W^{\rm ii}$	3.246 (4)	Rb2—O12$^{\rm vi}$	2.818 (4)
Rb1—O2$W^{\rm iii}$	3.109 (5)	Rb2—O11$^{\rm iv}$	2.863 (3)
Rb1—O1$W^{\rm iv}$	2.917 (4)	Rb2—O12$^{\rm vii}$	2.818 (4)
Rb1—O11$^{\rm iv}$	2.925 (3)		

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

Table 3
Selected bond lengths (Å) for (III).

Cs1—O1W	3.087 (9)	Cs1—O1$W^{\rm iii}$	3.400 (10)
Cs1—O2W	3.286 (13)	Cs2—O11	3.024 (8)
Cs1—O11	3.040 (8)	Cs2—O2$W^{\rm iv}$	3.324 (13)
Cs1—O1$W^{\rm i}$	3.400 (10)	Cs2—O12$^{\rm v}$	2.961 (9)
Cs1—O2$W^{\rm i}$	3.295 (12)	Cs2—O11$^{\rm ii}$	3.024 (8)
Cs1—O1$W^{\rm ii}$	3.087 (9)	Cs2—O12$^{\rm vi}$	2.961 (9)
Cs1—O11$^{\rm ii}$	3.040 (8)		

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

In all structures, two-dimensional coordination polymeric complex structures are generated, with the layers lying in the mirror planes parallel to (100). Fig. 4 shows the basic makeup of the layer in (I) while those for (II) or (III) are shown in Fig. 5. The water molecule O2W provides hydrogen-bonding links across the mirror plane to arsonate O13 acceptors (Tables 4, 5 and 6).

3. Supramolecular features

In the crystals of all three compounds, similar overall packing modes are observed, with the coordination polymeric layers lying along the mirror planes inter-linked across [100] through amine N4—H$\cdots$O hydrogen bonds to arsonate O13 and water O1W acceptors (Tables 4, 5 and 6). In this respect, they resemble the crystal packing of the Na p-arsanilate analogue (Smith & Wermuth, 2014) but the structure of that compound

Table 4
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4$^{\rm v}$	0.88 (6)	2.05 (6)	2.915 (7)	171 (5)
O1*W*—H12*W*···O11$^{\rm vi}$	0.89 (5)	1.77 (5)	2.660 (6)	175 (7)
O2*W*—H21*W*···O13$^{\rm vii}$	0.86 (5)	2.09 (6)	2.819 (6)	142 (6)
O12—H12···O13$^{\rm iv}$	0.87 (6)	1.70 (6)	2.538 (7)	160 (7)
N4—H41···O1*W*$^{\rm viii}$	0.86 (5)	2.17 (5)	3.010 (7)	164 (5)
N4—H42···O13$^{\rm ix}$	0.87 (6)	2.15 (6)	2.984 (7)	160 (5)

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

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4$^{\rm viii}$	0.89 (5)	2.04 (4)	2.923 (6)	176 (5)
O2*W*—H21*W*···O13$^{\rm ix}$	0.88 (4)	1.97 (4)	2.852 (5)	173 (5)
O12—H12···O13$^{\rm vii}$	0.86 (3)	1.73 (4)	2.552 (5)	158 (5)
N4—H41···O13$^{\rm x}$	0.86 (5)	2.18 (4)	3.022 (5)	167 (4)
N4—H42···O1*W*$^{\rm xi}$	0.88 (4)	2.13 (4)	3.005 (6)	176 (4)

Symmetry codes: (vii) $x, -y+1, z-\frac{1}{2}$; (viii) $-x+\frac{3}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (ix) $x, y, z-1$; (x) $-x+\frac{3}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (xi) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4$^{\rm vii}$	0.89 (9)	2.28 (13)	2.952 (13)	132 (10)
O2*W*—H21*W*···O13	0.89 (12)	2.16 (12)	2.850 (10)	134 (12)
O12—H12···O13$^{\rm vi}$	0.88 (5)	2.00 (12)	2.567 (13)	121 (12)
N4—H41···O1*W*$^{\rm viii}$	0.83 (14)	2.12 (15)	2.928 (15)	164 (9)
N4—H42···O13$^{\rm ix}$	0.91 (14)	2.20 (14)	3.082 (13)	166 (15)

Symmetry codes: (vi) $x, -y+1, z+\frac{1}{2}$; (vii) $-x+\frac{3}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (viii) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (ix) $-x+\frac{3}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

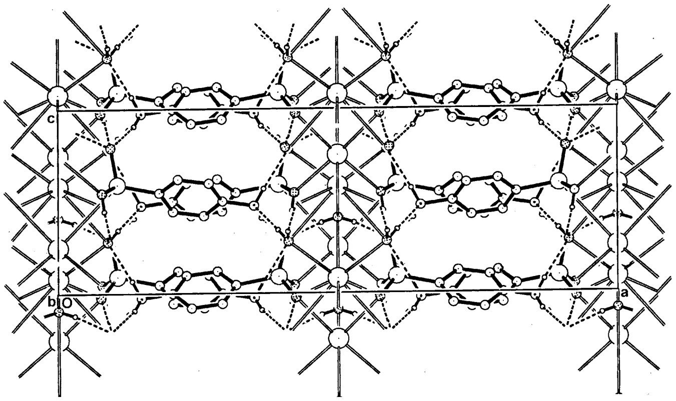


Figure 7
A view of the packing in the unit cell of (II) [or (III)] along [010], showing the associated cation/anion sheets linked peripherally across [100] by hydrogen bonds involving the amine groups.

(a trihydrate) differs from the current isotypic set in having significantly different coordination spheres, also lacking the mirror symmetry of the primary polymeric layers in (I)–(III). With these, the N4 amino group acts as an acceptor to an O1*W* hydrogen bond. The water molecule O1*W* also forms a hydrogen bond with O11$^{\rm vi}$ [symmetry code: (vi) $x, -y+2, z+\frac{1}{2}$] in (I), but not in (II) or (III). The protonated *p*-arsanilate O atom (O12) forms an intra-layer hydrogen bond with an O11 acceptor, giving overall three-dimensional network structures in all cases (Figs. 6 and 7). No *π*–*π* associations are present in the structures.

4. Database survey

Three-dimensional supramolecular structures involving complexes of hydrogen *p*-arsanilate and mixed metal types, as distinct from those involving uni-metal types, such as in (I)–(III) and in those examples which have been previously mentioned in the *Chemical context* section of this article, are worthy of noting here. Mixed-metal-ligand examples (Smith *et al.*, 2013) as well as mixed–metal structures add to the complexity of the coordination polymeric structures commonly generated, *e.g.* in the Mo/Ag, Mo/Cu and W/Na polyoxidometallate compounds (Johnson *et al.*, 2002), the Mo/V cage structure (Onet *et al.*, 2011) or the V/Na structure (Breen & Schmitt, 2008).

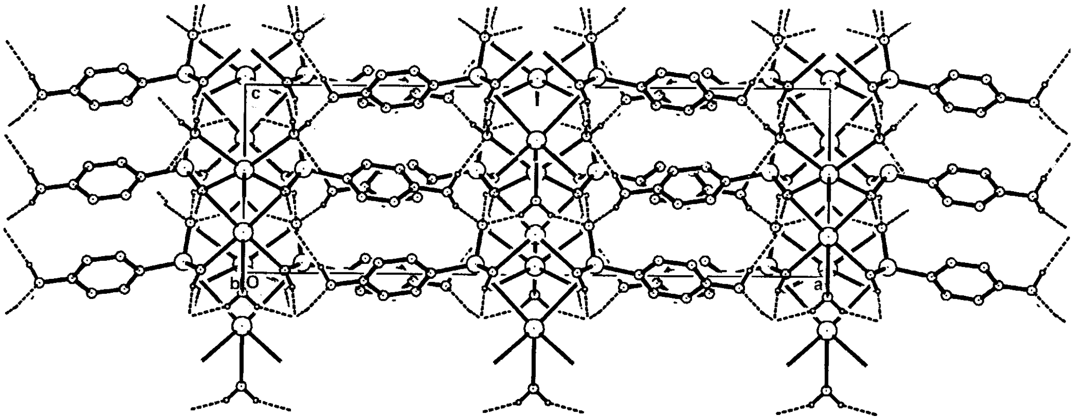


Figure 6
A view of the packing in the unit cell of (I) along [010], showing the associated cation/anion sheets linked peripherally across [100] by hydrogen bonds involving the anilinium amine groups. Hydrogen-bonding interactions are shown as dashed lines and aromatic H atoms have been omitted.

Table 7
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$[K_2(C_6H_7AsNO_3)_2(H_2O)_3]$	$[Rb_2(C_6H_7AsNO_3)_2(H_2O)_3]$	$[Cs_2(C_6H_7AsNO_3)_2(H_2O)_3]$
M_r	564.34	657.08	751.96
Crystal system, space group	Orthorhombic, $Cmc2_1$	Orthorhombic, $Cmc2_1$	Orthorhombic, $Cmc2_1$
Temperature (K)	200	200	200
a, b, c (Å)	24.3426 (18), 10.4266 (7), 7.8315 (6)	24.4783 (19), 10.4577 (9), 8.0978 (7)	24.650 (3), 10.4373 (9), 8.3992 (7)
V (Å^3)	1987.7 (3)	2072.9 (3)	2160.9 (4)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.83	7.94	6.46
Crystal size (mm)	0.35 × 0.22 × 0.11	0.35 × 0.20 × 0.12	0.40 × 0.22 × 0.10
Data collection			
Diffractometer	Oxford Diffraction Gemini-S CCD-detector	Oxford Diffraction Gemini-S CCD-detector	Oxford Diffraction Gemini-S CCD-detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.650, 0.980	0.375, 0.980	0.217, 0.980
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	2874, 1834, 1710	3623, 2093, 1899	4941, 1883, 1787
R_{int}	0.020	0.026	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.688	0.683	0.687
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.125, 1.23	0.032, 0.072, 1.03	0.041, 0.160, 1.18
No. of reflections	1834	2093	1883
No. of parameters	145	146	145
No. of restraints	8	8	8
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.84	0.70, −0.46	1.69, −1.00
Absolute structure	Flack (1983), 1281 Friedel pairs	Flack (1983), 1309 Friedel pairs	Flack (1983), 1405 Friedel pairs
Absolute structure parameter	0.03 (2)	−0.008 (12)	0.10 (4)

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

5. Synthesis and crystallization

Compounds (I)–(III) were synthesized by heating together for 5 min, 1 mmol quantities of 4-aminophenylarsonic acid and 0.5 mmol of either K_2CO_3 [for (I)], Rb_2CO_3 [for (II)] or Cs_2CO_3 [for (III)], in 20 ml of 50% ethanol/water (*v*/*v*). Room temperature evaporation of the solutions gave colourless crystal plates of the title compounds from which specimens were cleaved for the X-ray analyses.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 7. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods but their positional parameters were restrained in the refinement with N—H = 0.88 Å and O—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$. Other H atoms were included in the refinement at calculated positions, C—H = 0.95 Å, and treated as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Acknowledgements

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

References

Adelani, P. O., Jouffret, L. J., Szymanowski, J. E. S. & Burns, P. C. (2012). *Inorg. Chem.* **51**, 12032–12040.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Bosch, F. & Rosich, L. (2008). *Pharmacology*, **82**, 171–179.

Breen, J. M. & Schmitt, W. (2008). *Angew. Chem. Int. Ed.* **47**, 6904–6908.

Breen, J. M., Zhang, L., Clement, R. & Schmitt, W. (2012). *Inorg. Chem.* **51**, 19–21.

Chen, B., Wang, B., Lin, Z., Fan, L., Gao, Y., Chi, Y. & Hu, C. (2012). *Dalton Trans.* **41**, 6910–6913.

Ehrlich, P. & Bertheim, A. (1907). *Ber. Dtsch. Chem. Ges.* **40**, 3292–3297.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

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. Jr & Stein, A. (2002). *Inorg. Chem.* **41**, 2213–2218.

Khan, M. I., Chang, Y., Chen, Q., Hope, H., Parking, S., Goshorn, D. P. & Zubieta, J. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1197–1200.

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.

Liu, Z.-Q., Zhao, Y.-F., Huang, X.-H., Li, H.-H. & Huang, C.-C. (2010). *Chin. J. Struct. Chem.* **29**, 1724–1730.

Nuttall, R. H. & Hunter, W. N. (1996). *Acta Cryst.* C**52**, 1681–1683.

O'Neil, M. J. (2001). Editor. *The Merck Index*, 13th ed., p. 243. Whitehouse Station, NJ: Merck and Co., Inc.

Onet, C. I., Zhang, L., Clérac, R., Jean-Denis, J. B., Feeney, M., McCabe, T. M. & Schmitt, W. (2011). *Inorg. Chem.* **50**, 604–613.

Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd., Yarnton, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shimada, A. (1961). *Bull. Chem. Soc. Jpn*, **34**, 639–643.

Smith, T. M., Strauskulage, L., Perrin, K. A. & Zubieta, J. (2013). *Inorg. Chim. Acta*, **407**, 48–57.

Smith, G. & Wermuth, U. D. (2014). *Acta Cryst.* C**70**, 738–741.

Smith, G. & Wermuth, U. D. (2017). *Acta Cryst.* C**73**, 61–67.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Steverding, D. (2010). *Parasites & Vectors*, **3**, 15.

Xiao, Z.-P., Wen, M., Wang, C.-Y. & Huang, X.-H. (2015). *Acta Cryst.* C**71**, 258–261.

Xie, Y.-P., Yang, J., Ma, J.-F., Zhang, L.-P., Song, S.-Y. & Su, Z.-M. (2008). *Chem. Eur. J.* **14**, 4093–4103.

supporting information

Acta Cryst. (2017). E**73**, 203-208 [https://doi.org/10.1107/S2056989017000445]

Crystal structures and hydrogen bonding in the isotypic series of hydrated alkali metal (K, Rb and Cs) complexes with 4-aminophenylarsonic acid

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: *SIR92* (Altomare *et al.*, 1993); 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) Poly[di-μ_3-4-aminophenylarsonato-tri-μ_2-aqua-dipotassium]

Crystal data

$[K_2(C_6H_7AsNO_3)_2(H_2O)_3]$
$M_r = 564.34$
Orthorhombic, $Cmc2_1$
Hall symbol: C 2c -2
$a = 24.3426$ (18) Å
$b = 10.4266$ (7) Å
$c = 7.8315$ (6) Å
$V = 1987.7$ (3) Å^3
$Z = 4$

$F(000) = 1128$
$D_x = 1.886$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1421 reflections
$\theta = 4.1$–28.7°
$\mu = 3.83$ mm^{-1}
$T = 200$ K
Prism, colourless
0.35 × 0.22 × 0.11 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)
$T_{min} = 0.650$, $T_{max} = 0.980$

2874 measured reflections
1834 independent reflections
1710 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 29.3°$, $\theta_{min} = 3.2°$
$h = -32 \rightarrow 17$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.125$
$S = 1.23$
1834 reflections
145 parameters
8 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

$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}
Absolute structure: Flack (1983), 1281 Friedel pairs
Absolute structure parameter: 0.03 (2)

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 > 2sigma(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	0.60155 (2)	0.63813 (4)	0.55509 (10)	0.0164 (2)
K1	0.50000	0.94523 (15)	0.5457 (3)	0.0224 (4)
K2	0.50000	0.63621 (19)	0.2140 (3)	0.0279 (6)
O1W	0.5845 (2)	1.0465 (4)	0.7396 (6)	0.0260 (12)
O2W	0.50000	0.7951 (6)	−0.1067 (9)	0.0263 (19)
O11	0.57103 (16)	0.7477 (4)	0.4358 (6)	0.0227 (12)
O12	0.5720 (2)	0.4898 (4)	0.5138 (6)	0.0333 (16)
O13	0.59063 (19)	0.6581 (4)	0.7630 (7)	0.0247 (14)
N4	0.8483 (2)	0.6311 (5)	0.4372 (8)	0.0243 (17)
C1	0.6778 (3)	0.6280 (5)	0.5052 (8)	0.0197 (16)
C2	0.7027 (3)	0.7225 (5)	0.4072 (8)	0.0203 (16)
C3	0.7583 (3)	0.7230 (5)	0.3828 (8)	0.0230 (17)
C4	0.7918 (3)	0.6313 (5)	0.4615 (7)	0.0170 (17)
C5	0.7669 (2)	0.5344 (4)	0.5574 (10)	0.0203 (14)
C6	0.7104 (2)	0.5332 (5)	0.5803 (8)	0.0197 (16)
H2	0.68080	0.78760	0.35650	0.0240*
H3	0.77440	0.78640	0.31150	0.0270*
H5	0.78880	0.46900	0.60720	0.0240*
H6	0.69380	0.46780	0.64730	0.0240*
H11W	0.608 (2)	0.998 (6)	0.795 (9)	0.0300*
H12	0.585 (3)	0.450 (6)	0.425 (6)	0.0300*
H12W	0.582 (3)	1.116 (4)	0.806 (8)	0.0300*
H21W	0.525 (2)	0.781 (7)	−0.181 (7)	0.0300*
H41	0.866 (3)	0.622 (5)	0.532 (5)	0.0240*
H42	0.863 (3)	0.683 (6)	0.363 (7)	0.0240*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0178 (3)	0.0148 (3)	0.0167 (3)	−0.0020 (2)	0.0030 (3)	−0.0007 (3)
K1	0.0198 (7)	0.0217 (7)	0.0256 (8)	0.0000	0.0000	−0.0055 (9)
K2	0.0186 (9)	0.0387 (11)	0.0264 (10)	0.0000	0.0000	−0.0114 (8)

O1W	0.028 (2)	0.023 (2)	0.027 (2)	0.0021 (19)	−0.006 (2)	−0.001 (2)
O2W	0.018 (3)	0.027 (3)	0.034 (4)	0.0000	0.0000	−0.003 (3)
O11	0.019 (2)	0.026 (2)	0.023 (2)	−0.0026 (17)	0.0023 (18)	0.0053 (18)
O12	0.037 (3)	0.022 (2)	0.041 (3)	−0.0120 (19)	0.022 (2)	−0.014 (2)
O13	0.023 (2)	0.024 (2)	0.027 (3)	0.0033 (19)	0.008 (2)	0.004 (2)
N4	0.019 (3)	0.024 (3)	0.030 (3)	0.002 (2)	−0.001 (2)	0.002 (2)
C1	0.022 (3)	0.015 (2)	0.022 (3)	−0.001 (2)	0.001 (2)	−0.002 (2)
C2	0.022 (3)	0.017 (2)	0.022 (3)	0.007 (2)	−0.001 (2)	0.000 (2)
C3	0.026 (3)	0.018 (3)	0.025 (3)	−0.003 (2)	0.006 (2)	0.011 (3)
C4	0.025 (3)	0.021 (3)	0.005 (3)	0.005 (2)	0.005 (2)	−0.0027 (19)
C5	0.025 (2)	0.013 (2)	0.023 (3)	0.0061 (18)	−0.002 (3)	0.003 (3)
C6	0.024 (3)	0.016 (2)	0.019 (3)	0.0002 (19)	0.007 (2)	0.001 (2)

Geometric parameters (Å, º)

K1—O1W	2.766 (5)	O2W—H21W	0.86 (5)
K1—O11	2.824 (4)	O2W—H21W^{ii}	0.86 (5)
K1—O2W^{i}	2.959 (7)	O12—H12	0.87 (6)
K1—O1W^{ii}	2.766 (5)	N4—C4	1.389 (9)
K1—O11^{ii}	2.824 (4)	N4—H41	0.86 (5)
K2—O2W	3.009 (7)	N4—H42	0.87 (6)
K2—O11	2.713 (5)	C1—C2	1.388 (8)
K2—O12^{iii}	2.694 (5)	C1—C6	1.397 (8)
K2—O11^{ii}	2.713 (5)	C2—C3	1.367 (10)
K2—O12^{iv}	2.694 (5)	C3—C4	1.400 (9)
As1—O11	1.652 (4)	C4—C5	1.397 (8)
As1—O12	1.736 (4)	C5—C6	1.387 (7)
As1—O13	1.663 (5)	C2—H2	0.9500
As1—C1	1.900 (7)	C3—H3	0.9500
O1W—H11W	0.88 (6)	C5—H5	0.9500
O1W—H12W	0.89 (5)	C6—H6	0.9500
O11—As1—O12	108.9 (2)	K1—O1W—H12W	125 (5)
O11—As1—O13	113.3 (2)	H11W—O1W—H12W	103 (6)
O11—As1—C1	111.2 (2)	K1^{v}—O2W—H21W	116 (5)
O12—As1—O13	103.2 (2)	H21W—O2W—H21W^{ii}	91 (5)
O12—As1—C1	108.5 (2)	K1^{v}—O2W—H21W^{ii}	116 (5)
O13—As1—C1	111.4 (3)	K2—O2W—H21W	118 (4)
O1W—K1—O11	89.45 (13)	K2—O2W—H21W^{ii}	118 (4)
O1W—K1—O2W^{i}	82.66 (13)	K2^{vi}—O12—H12	118 (4)
O1W—K1—O1W^{ii}	96.08 (15)	As1—O12—H12	115 (4)
O1W—K1—O11^{ii}	154.31 (14)	C4—N4—H41	112 (4)
O2W^{i}—K1—O11	122.99 (14)	H41—N4—H42	116 (6)
O1W^{ii}—K1—O11	154.31 (14)	C4—N4—H42	120 (5)
O11—K1—O11^{ii}	75.52 (12)	As1—C1—C6	120.5 (4)
O1W^{ii}—K1—O2W^{i}	82.66 (13)	As1—C1—C2	120.1 (5)
O2W^{i}—K1—O11^{ii}	122.99 (14)	C2—C1—C6	119.1 (6)
O1W^{ii}—K1—O11^{ii}	89.45 (13)	C1—C2—C3	120.8 (6)

O2W—K2—O11	107.37 (14)	C2—C3—C4	120.9 (6)
O2W—K2—O12^{iii}	77.45 (14)	C3—C4—C5	118.6 (6)
O2W—K2—O11^{ii}	107.37 (14)	N4—C4—C3	121.2 (5)
O2W—K2—O12^{iv}	77.45 (14)	N4—C4—C5	120.2 (5)
O11—K2—O12^{iii}	175.18 (16)	C4—C5—C6	120.4 (5)
O11—K2—O11^{ii}	79.20 (14)	C1—C6—C5	120.2 (5)
O11—K2—O12^{iv}	99.61 (13)	C1—C2—H2	120.00
O11^{ii}—K2—O12^{iii}	99.61 (13)	C3—C2—H2	120.00
O12^{iii}—K2—O12^{iv}	81.18 (15)	C2—C3—H3	120.00
O11^{ii}—K2—O12^{iv}	175.18 (16)	C4—C3—H3	120.00
K1^{v}—O2W—K2	99.6 (2)	C4—C5—H5	120.00
K1—O11—K2	96.75 (13)	C6—C5—H5	120.00
As1—O12—K2^{vi}	126.6 (2)	C1—C6—H6	120.00
K1—O1W—H11W	122 (4)	C5—C6—H6	120.00

O12—As1—O11—K1	109.9 (3)	O11^{ii}—K1—O11—K2	25.38 (14)
O12—As1—O11—K2	−6.6 (3)	O1W—K1—O11^{ii}—K2	−81.4 (4)
O13—As1—O11—K1	−4.3 (3)	O11—K1—O11^{ii}—K2	−25.38 (14)
O13—As1—O11—K2	−120.8 (2)	O2W—K2—O11—As1	−146.8 (2)
C1—As1—O11—K1	−130.6 (3)	O2W—K2—O11—K1	78.91 (15)
C1—As1—O11—K2	112.9 (2)	O11^{ii}—K2—O11—As1	108.2 (2)
O11—As1—O12—K2^{vi}	−103.8 (3)	O11^{ii}—K2—O11—K1	−26.09 (14)
O13—As1—O12—K2^{vi}	16.9 (3)	O12^{iv}—K2—O11—As1	−67.1 (2)
C1—As1—O12—K2^{vi}	135.1 (3)	O12^{iv}—K2—O11—K1	158.66 (14)
O11—As1—C1—C2	12.4 (6)	O11—K2—O11^{ii}—K1	26.09 (14)
O11—As1—C1—C6	−174.0 (5)	As1—C1—C2—C3	174.1 (5)
O12—As1—C1—C2	132.2 (5)	C6—C1—C2—C3	0.5 (9)
O12—As1—C1—C6	−54.3 (5)	As1—C1—C6—C5	−173.3 (5)
O13—As1—C1—C2	−114.9 (5)	C2—C1—C6—C5	0.3 (9)
O13—As1—C1—C6	58.6 (5)	C1—C2—C3—C4	−2.6 (9)
O1W—K1—O11—As1	61.8 (3)	C2—C3—C4—N4	179.9 (6)
O1W—K1—O11—K2	−175.68 (15)	C2—C3—C4—C5	3.8 (9)
O2W^{i}—K1—O11—As1	142.7 (2)	N4—C4—C5—C6	−179.2 (6)
O1W^{ii}—K1—O11—As1	−41.1 (5)	C3—C4—C5—C6	−3.0 (9)
O1W^{ii}—K1—O11—K2	81.4 (4)	C4—C5—C6—C1	1.0 (9)
O11^{ii}—K1—O11—As1	−97.1 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4^{vii}	0.88 (6)	2.05 (6)	2.915 (7)	171 (5)
O1*W*—H12*W*···O11^{viii}	0.89 (5)	1.77 (5)	2.660 (6)	175 (7)
O2*W*—H21*W*···O13^{ix}	0.86 (5)	2.09 (6)	2.819 (6)	142 (6)
O12—H12···O13^{iv}	0.87 (6)	1.70 (6)	2.538 (7)	160 (7)

N4—H41···O1*W*^{x}	0.86 (5)	2.17 (5)	3.010 (7)	164 (5)
N4—H42···O13^{xi}	0.87 (6)	2.15 (6)	2.984 (7)	160 (5)

Symmetry codes: (iv) *x*, −*y*+1, *z*−1/2; (vii) −*x*+3/2, −*y*+3/2, *z*+1/2; (viii) *x*, −*y*+2, *z*+1/2; (ix) *x*, *y*, *z*−1; (x) −*x*+3/2, *y*−1/2, *z*; (xi) −*x*+3/2, −*y*+3/2, *z*−1/2.

(II) Poly[di-μ_3-4-aminophenylarsonato-tri-μ_2-aqua-dirubidium]

Crystal data

$[Rb_2(C_6H_7AsNO_3)_2(H_2O)_3]$	$F(000) = 1272$
$M_r = 657.08$	$D_x = 2.105$ Mg m^{-3}
Orthorhombic, *Cmc*2$_1$	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: C 2c -2	Cell parameters from 1374 reflections
$a = 24.4783$ (19) Å	$\theta = 4.0$–28.7°
$b = 10.4577$ (9) Å	$\mu = 7.94$ mm^{-1}
$c = 8.0978$ (7) Å	$T = 200$ K
$V = 2072.9$ (3) Å^3	Prism, colourless
$Z = 4$	0.35 × 0.20 × 0.12 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	3623 measured reflections
Radiation source: Enhance (Mo) X-ray source	2093 independent reflections
Graphite monochromator	1899 reflections with $I > 2\sigma(I)$
Detector resolution: 16.077 pixels mm^{-1}	$R_{int} = 0.026$
ω scans	$\theta_{max} = 29.0°$, $\theta_{min} = 3.9°$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)	$h = -33 \rightarrow 15$
$T_{min} = 0.375$, $T_{max} = 0.980$	$k = -14 \rightarrow 13$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$(\Delta/\sigma)_{max} = 0.003$
$wR(F^2) = 0.072$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.46$ e Å^{-3}
2093 reflections	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
146 parameters	Extinction coefficient: 0.00306 (19)
8 restraints	Absolute structure: Flack (1983), 1309 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: −0.008 (12)
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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 > 2sigma(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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Rb1	0.50000	0.94747 (5)	0.57916 (11)	0.0264 (2)
Rb2	0.50000	0.63207 (8)	0.24818 (10)	0.0376 (3)
As1	0.60556 (2)	0.63552 (4)	0.58879 (6)	0.0200 (1)
O1W	0.58793 (16)	1.0545 (3)	0.7791 (5)	0.0333 (11)
O2W	0.50000	0.7864 (5)	−0.0920 (7)	0.0337 (17)
O11	0.57535 (14)	0.7458 (3)	0.4753 (4)	0.0302 (11)
O12	0.57765 (17)	0.4882 (3)	0.5436 (5)	0.0404 (13)
O13	0.59344 (15)	0.6516 (3)	0.7898 (4)	0.0275 (11)
N4	0.85111 (17)	0.6329 (4)	0.4734 (6)	0.0287 (16)
C1	0.68166 (19)	0.6279 (4)	0.5443 (6)	0.0200 (14)
C2	0.7060 (2)	0.7197 (5)	0.4430 (6)	0.0250 (16)
C3	0.7614 (2)	0.7222 (5)	0.4197 (7)	0.0270 (17)
C4	0.7946 (2)	0.6315 (4)	0.4982 (6)	0.0230 (16)
C5	0.77044 (19)	0.5380 (4)	0.5957 (8)	0.0270 (14)
C6	0.7146 (2)	0.5357 (4)	0.6178 (6)	0.0260 (16)
H2	0.68380	0.78150	0.38940	0.0300*
H3	0.77730	0.78530	0.35030	0.0320*
H5	0.79260	0.47510	0.64760	0.0320*
H6	0.69850	0.47060	0.68370	0.0310*
H11W	0.6067 (19)	1.001 (4)	0.842 (6)	0.0370*
H12	0.582 (2)	0.459 (5)	0.445 (3)	0.0370*
H12W	0.589 (3)	1.127 (3)	0.833 (6)	0.0370*
H21W	0.5290 (15)	0.741 (4)	−0.120 (7)	0.0370*
H41	0.864 (2)	0.689 (4)	0.407 (6)	0.0300*
H42	0.8680 (19)	0.613 (4)	0.566 (4)	0.0300*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0241 (3)	0.0282 (3)	0.0268 (3)	0.0000	0.0000	−0.0051 (4)
Rb2	0.0227 (4)	0.0597 (5)	0.0304 (4)	0.0000	0.0000	−0.0179 (4)
As1	0.0210 (2)	0.0183 (2)	0.0206 (2)	−0.0019 (2)	0.0036 (2)	−0.0007 (3)
O1W	0.032 (2)	0.0309 (19)	0.037 (2)	−0.0008 (16)	−0.0036 (19)	−0.0005 (18)
O2W	0.032 (3)	0.027 (3)	0.042 (3)	0.0000	0.0000	−0.006 (2)
O11	0.0206 (19)	0.037 (2)	0.033 (2)	−0.0005 (16)	−0.0041 (16)	0.0069 (16)
O12	0.046 (2)	0.0303 (18)	0.045 (3)	−0.0176 (17)	0.0261 (19)	−0.0182 (19)
O13	0.036 (2)	0.0257 (18)	0.0207 (18)	0.0053 (15)	0.0064 (16)	0.0031 (15)
N4	0.019 (2)	0.035 (3)	0.032 (3)	0.0024 (18)	0.0042 (19)	0.006 (2)
C1	0.019 (2)	0.021 (2)	0.020 (3)	0.0003 (17)	0.0009 (18)	−0.0017 (18)
C2	0.025 (3)	0.021 (2)	0.029 (3)	0.001 (2)	0.002 (2)	0.005 (2)
C3	0.023 (3)	0.025 (3)	0.033 (3)	0.001 (2)	0.006 (2)	0.009 (2)
C4	0.025 (3)	0.021 (2)	0.023 (3)	0.0018 (19)	0.004 (2)	−0.0043 (19)
C5	0.031 (2)	0.020 (2)	0.030 (3)	0.0078 (17)	0.003 (3)	0.003 (3)
C6	0.036 (3)	0.018 (2)	0.024 (3)	−0.0023 (19)	0.006 (2)	0.0040 (19)

Geometric parameters (Å, º)

Rb1—O1W	2.917 (4)	O1W—H12W	0.88 (4)
Rb1—O11	2.925 (3)	O2W—H21W	0.88 (4)
Rb1—O2W^{i}	3.151 (6)	O2W—H21W^{iv}	0.88 (4)
Rb1—O1W^{ii}	3.246 (4)	O12—H12	0.86 (3)
Rb1—O2W^{iii}	3.109 (5)	N4—C4	1.398 (6)
Rb1—O1W^{iv}	2.917 (4)	N4—H41	0.86 (5)
Rb1—O11^{iv}	2.925 (3)	N4—H42	0.88 (4)
Rb1—O1W^{v}	3.246 (4)	C1—C2	1.396 (7)
Rb2—O2W	3.193 (6)	C1—C6	1.391 (6)
Rb2—O11	2.863 (3)	C2—C3	1.369 (7)
Rb2—O12^{vi}	2.818 (4)	C3—C4	1.402 (7)
Rb2—O11^{iv}	2.863 (3)	C4—C5	1.389 (7)
Rb2—O12^{vii}	2.818 (4)	C5—C6	1.379 (7)
As1—O11	1.650 (3)	C2—H2	0.9500
As1—O12	1.725 (3)	C3—H3	0.9500
As1—O13	1.663 (3)	C5—H5	0.9500
As1—C1	1.899 (5)	C6—H6	0.9500
O1W—H11W	0.89 (5)		

O1W—Rb1—O11	88.34 (10)	Rb1—O1W—Rb1^{iii}	85.63 (10)
O1W—Rb1—O2W^{i}	74.69 (10)	Rb1^{viii}—O2W—Rb2	178.05 (19)
O1W—Rb1—O1W^{ii}	155.13 (9)	Rb1^{ii}—O2W—Rb2	93.89 (15)
O1W—Rb1—O2W^{iii}	84.49 (10)	Rb1^{viii}—O2W—Rb1^{ii}	84.16 (13)
O1W—Rb1—O1W^{iv}	95.12 (11)	Rb1—O11—Rb2	94.47 (10)
O1W—Rb1—O11^{iv}	154.37 (10)	Rb1—O11—As1	128.79 (16)
O1W—Rb1—O1W^{v}	85.91 (10)	Rb2—O11—As1	110.86 (15)
O2W^{i}—Rb1—O11	81.81 (10)	Rb2^{ix}—O12—As1	122.77 (19)
O1W^{ii}—Rb1—O11	101.44 (9)	Rb1^{iii}—O1W—H12W	70 (4)
O2W^{iii}—Rb1—O11	121.14 (10)	Rb1—O1W—H12W	129 (5)
O1W^{iv}—Rb1—O11	154.37 (10)	H11W—O1W—H12W	104 (5)
O11—Rb1—O11^{iv}	78.18 (9)	Rb1—O1W—H11W	117 (3)
O1W^{v}—Rb1—O11	50.37 (9)	Rb1^{iii}—O1W—H11W	85 (3)
O1W^{ii}—Rb1—O2W^{i}	128.99 (8)	Rb2—O2W—H21W^{iv}	87 (4)
O2W^{i}—Rb1—O2W^{iii}	148.79 (14)	Rb1^{viii}—O2W—H21W	94 (4)
O1W^{iv}—Rb1—O2W^{i}	74.69 (10)	Rb2—O2W—H21W	87 (4)
O2W^{i}—Rb1—O11^{iv}	81.81 (10)	H21W—O2W—H21W^{iv}	107 (4)
O1W^{v}—Rb1—O2W^{i}	128.99 (8)	Rb1^{viii}—O2W—H21W^{iv}	94 (4)
O1W^{ii}—Rb1—O2W^{iii}	70.85 (9)	Rb1^{ii}—O2W—H21W	127 (3)
O1W^{ii}—Rb1—O1W^{iv}	85.91 (10)	Rb1^{ii}—O2W—H21W^{iv}	127 (3)
O1W^{ii}—Rb1—O11^{iv}	50.37 (9)	Rb2^{ix}—O12—H12	118 (3)
O1W^{ii}—Rb1—O1W^{v}	83.07 (10)	As1—O12—H12	118 (3)
O1W^{iv}—Rb1—O2W^{iii}	84.49 (10)	C4—N4—H41	118 (3)
O2W^{iii}—Rb1—O11^{iv}	121.14 (10)	C4—N4—H42	110 (3)
O1W^{v}—Rb1—O2W^{iii}	70.85 (9)	H41—N4—H42	122 (4)
O1W^{iv}—Rb1—O11^{iv}	88.34 (10)	C2—C1—C6	118.7 (4)
O1W^{iv}—Rb1—O1W^{v}	155.13 (9)	As1—C1—C2	120.1 (3)

O1W^{v}—Rb1—O11^{iv}	101.44 (9)	As1—C1—C6	121.1 (3)
O2W—Rb2—O11	110.13 (10)	C1—C2—C3	121.1 (5)
O2W—Rb2—O12^{vi}	73.64 (10)	C2—C3—C4	119.9 (5)
O2W—Rb2—O11^{iv}	110.13 (10)	N4—C4—C5	120.7 (4)
O2W—Rb2—O12^{vii}	73.64 (10)	N4—C4—C3	120.1 (4)
O11—Rb2—O12^{vi}	176.01 (11)	C3—C4—C5	119.2 (4)
O11—Rb2—O11^{iv}	80.20 (10)	C4—C5—C6	120.5 (4)
O11—Rb2—O12^{vii}	97.38 (11)	C1—C6—C5	120.5 (4)
O11^{iv}—Rb2—O12^{vi}	97.38 (11)	C1—C2—H2	119.00
O12^{vi}—Rb2—O12^{vii}	84.84 (12)	C3—C2—H2	119.00
O11^{iv}—Rb2—O12^{vii}	176.01 (11)	C2—C3—H3	120.00
O11—As1—O12	109.20 (17)	C4—C3—H3	120.00
O11—As1—O13	113.24 (16)	C4—C5—H5	120.00
O11—As1—C1	111.30 (18)	C6—C5—H5	120.00
O12—As1—O13	103.14 (18)	C1—C6—H6	120.00
O12—As1—C1	108.11 (19)	C5—C6—H6	120.00
O13—As1—C1	111.40 (19)		

O11—Rb1—O1W—Rb1^{iii}	−128.95 (9)	O13—As1—O11—Rb1	−4.5 (3)
O1W—Rb1—O11—Rb2	−175.57 (10)	O13—As1—O11—Rb2	−118.92 (17)
O1W—Rb1—O11—As1	63.0 (2)	C1—As1—O11—Rb1	−130.9 (2)
O2W^{i}—Rb1—O11—As1	−11.8 (2)	C1—As1—O11—Rb2	114.66 (18)
O1W^{ii}—Rb1—O11—Rb2	−18.62 (11)	O11—As1—O12—Rb2^{ix}	−101.6 (2)
O1W^{ii}—Rb1—O11—As1	−140.0 (2)	O13—As1—O12—Rb2^{ix}	19.1 (2)
O2W^{iii}—Rb1—O11—As1	145.56 (19)	C1—As1—O12—Rb2^{ix}	137.2 (2)
O1W^{iv}—Rb1—O11—Rb2	86.1 (2)	O11—As1—C1—C2	7.8 (4)
O1W^{iv}—Rb1—O11—As1	−35.4 (4)	O11—As1—C1—C6	−175.6 (4)
O11^{iv}—Rb1—O11—Rb2	26.37 (9)	O12—As1—C1—C2	127.7 (4)
O11^{iv}—Rb1—O11—As1	−95.1 (2)	O12—As1—C1—C6	−55.6 (4)
O1W^{v}—Rb1—O11—Rb2	−89.51 (13)	O13—As1—C1—C2	−119.7 (4)
O1W^{v}—Rb1—O11—As1	149.1 (3)	O13—As1—C1—C6	57.0 (4)
O1W—Rb1—O11^{iv}—Rb2	−86.1 (2)	As1—C1—C2—C3	174.8 (4)
O11—Rb1—O11^{iv}—Rb2	−26.37 (9)	C6—C1—C2—C3	−2.0 (7)
O2W—Rb2—O11—Rb1	81.20 (11)	As1—C1—C6—C5	−174.4 (4)
O2W—Rb2—O11—As1	−144.19 (15)	C2—C1—C6—C5	2.4 (7)
O11^{iv}—Rb2—O11—Rb1	−26.79 (9)	C1—C2—C3—C4	0.0 (8)
O11^{iv}—Rb2—O11—As1	107.83 (17)	C2—C3—C4—N4	179.3 (5)
O12^{vii}—Rb2—O11—Rb1	156.43 (10)	C2—C3—C4—C5	1.6 (8)
O12^{vii}—Rb2—O11—As1	−68.96 (17)	N4—C4—C5—C6	−179.0 (5)
O11—Rb2—O11^{iv}—Rb1	26.79 (9)	C3—C4—C5—C6	−1.3 (8)
O12—As1—O11—Rb1	109.8 (2)	C4—C5—C6—C1	−0.8 (8)
O12—As1—O11—Rb2	−4.6 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4^{x}	0.89 (5)	2.04 (4)	2.923 (6)	176 (5)
O2*W*—H21*W*···O13^{viii}	0.88 (4)	1.97 (4)	2.852 (5)	173 (5)
O12—H12···O13^{vii}	0.86 (3)	1.73 (4)	2.552 (5)	158 (5)
N4—H41···O13^{xi}	0.86 (5)	2.18 (4)	3.022 (5)	167 (4)
N4—H42···O1*W*^{xii}	0.88 (4)	2.13 (4)	3.005 (6)	176 (4)

Symmetry codes: (vii) *x*, −*y*+1, *z*−1/2; (viii) *x*, *y*, *z*−1; (x) −*x*+3/2, −*y*+3/2, *z*+1/2; (xi) −*x*+3/2, −*y*+3/2, *z*−1/2; (xii) −*x*+3/2, *y*−1/2, *z*.

(III) Poly[di-μ_3-4-aminophenylarsonato-tri-μ_2-aqua-dicaesium]

Crystal data

$[Cs_2(C_6H_7AsNO_3)_2(H_2O)_3]$	$F(000) = 1416$
$M_r = 751.96$	$D_x = 2.311$ Mg m^{-3}
Orthorhombic, *Cmc*2$_1$	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: C 2c -2	Cell parameters from 1999 reflections
$a = 24.650$ (3) Å	$\theta = 4.0$–28.9°
$b = 10.4373$ (9) Å	$\mu = 6.46$ mm^{-1}
$c = 8.3992$ (7) Å	$T = 200$ K
$V = 2160.9$ (4) Å^3	Prism, colourless
$Z = 4$	0.40 × 0.22 × 0.10 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	4941 measured reflections
Radiation source: Enhance Mo X-ray source	1883 independent reflections
Graphite monochromator	1787 reflections with $I > 2\sigma(I)$
Detector resolution: 16.077 pixels mm^{-1}	$R_{int} = 0.030$
ω scans	$\theta_{max} = 29.3°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)	$h = -33 \rightarrow 29$
$T_{min} = 0.217$, $T_{max} = 0.980$	$k = -14 \rightarrow 13$
	$l = -11 \rightarrow 6$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.1178P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.160$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.18$	$\Delta\rho_{max} = 1.69$ e Å^{-3}
1883 reflections	$\Delta\rho_{min} = -1.00$ e Å^{-3}
145 parameters	Absolute structure: Flack (1983), 1405 Friedel pairs
8 restraints	Absolute structure parameter: 0.10 (4)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cs1	0.50000	0.95299 (7)	0.67229 (13)	0.0217 (2)
Cs2	0.50000	0.62982 (10)	0.99928 (13)	0.0311 (3)
As1	0.61041 (4)	0.63299 (7)	0.65867 (12)	0.0166 (3)
O1W	0.5936 (4)	1.0619 (7)	0.4690 (11)	0.026 (3)
O2W	0.50000	0.7680 (11)	0.3558 (16)	0.027 (3)
O11	0.5799 (3)	0.7443 (8)	0.7661 (11)	0.028 (3)
O12	0.5841 (4)	0.4827 (8)	0.7086 (11)	0.036 (3)
O13	0.5962 (3)	0.6457 (7)	0.4668 (11)	0.024 (2)
N4	0.8542 (4)	0.6351 (9)	0.7686 (14)	0.025 (3)
C1	0.6861 (5)	0.6283 (7)	0.6996 (13)	0.016 (3)
C2	0.7088 (5)	0.7189 (9)	0.7999 (14)	0.022 (3)
C3	0.7634 (5)	0.7201 (9)	0.8256 (18)	0.025 (3)
C4	0.7983 (5)	0.6344 (9)	0.7490 (14)	0.022 (3)
C5	0.7752 (5)	0.5399 (9)	0.6487 (19)	0.031 (4)
C6	0.7202 (5)	0.5380 (8)	0.6236 (15)	0.023 (3)
H2	0.68620	0.78020	0.85100	0.0260*
H3	0.77820	0.78100	0.89760	0.0300*
H5	0.79770	0.47800	0.59880	0.0370*
H6	0.70480	0.47550	0.55480	0.0270*
H11W	0.624 (3)	1.039 (12)	0.420 (15)	0.0340*
H12	0.578 (7)	0.493 (15)	0.811 (5)	0.0340*
H12W	0.589 (4)	1.126 (12)	0.400 (12)	0.0340*
H21W	0.529 (4)	0.773 (13)	0.418 (16)	0.0340*
H41	0.865 (6)	0.602 (12)	0.685 (18)	0.0270*
H42	0.870 (6)	0.706 (11)	0.81 (2)	0.0270*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0185 (4)	0.0261 (4)	0.0204 (4)	0.0000	0.0000	0.0024 (4)
Cs2	0.0174 (5)	0.0525 (6)	0.0233 (5)	0.0000	0.0000	0.0136 (5)
As1	0.0146 (5)	0.0182 (4)	0.0169 (5)	−0.0016 (3)	−0.0029 (5)	0.0004 (4)
O1W	0.017 (4)	0.035 (4)	0.026 (5)	0.000 (3)	0.009 (4)	0.002 (4)
O2W	0.020 (6)	0.031 (5)	0.030 (7)	0.0000	0.0000	0.002 (5)
O11	0.020 (4)	0.032 (4)	0.031 (5)	−0.002 (3)	0.007 (4)	−0.005 (3)
O12	0.042 (5)	0.033 (4)	0.032 (5)	−0.021 (4)	−0.024 (4)	0.007 (4)
O13	0.019 (4)	0.029 (4)	0.025 (4)	0.005 (3)	0.000 (4)	0.001 (3)
N4	0.020 (5)	0.026 (4)	0.030 (5)	0.003 (3)	−0.015 (5)	−0.004 (4)
C1	0.019 (5)	0.015 (4)	0.014 (4)	0.000 (3)	−0.004 (4)	0.001 (3)
C2	0.027 (6)	0.020 (4)	0.019 (5)	0.006 (4)	−0.009 (4)	−0.011 (4)

C3	0.022 (5)	0.024 (4)	0.030 (6)	0.003 (4)	0.006 (6)	−0.002 (5)
C4	0.021 (6)	0.021 (4)	0.023 (6)	0.004 (4)	0.002 (5)	0.006 (4)
C5	0.028 (6)	0.024 (4)	0.041 (8)	0.006 (4)	−0.005 (6)	−0.013 (5)
C6	0.020 (5)	0.020 (4)	0.029 (6)	−0.003 (3)	−0.005 (5)	−0.002 (4)

Geometric parameters (Å, º)

Cs1—O1W	3.087 (9)	O1W—H12W	0.89 (12)
Cs1—O2W	3.286 (13)	O2W—H21W	0.89 (12)
Cs1—O11	3.040 (8)	O2W—H21W^{ii}	0.89 (12)
Cs1—O1W^{i}	3.400 (10)	O12—H12	0.88 (5)
Cs1—O2W^{i}	3.295 (12)	N4—C4	1.388 (16)
Cs1—O1W^{ii}	3.087 (9)	N4—H41	0.83 (14)
Cs1—O11^{ii}	3.040 (8)	N4—H42	0.91 (14)
Cs1—O1W^{iii}	3.400 (10)	C1—C2	1.385 (15)
Cs2—O11	3.024 (8)	C1—C6	1.415 (15)
Cs2—O2W^{iv}	3.324 (13)	C2—C3	1.363 (17)
Cs2—O12^{v}	2.961 (9)	C3—C4	1.398 (16)
Cs2—O11^{ii}	3.024 (8)	C4—C5	1.417 (17)
Cs2—O12^{vi}	2.961 (9)	C5—C6	1.372 (18)
As1—O11	1.652 (9)	C2—H2	0.9500
As1—O12	1.748 (9)	C3—H3	0.9500
As1—O13	1.655 (9)	C5—H5	0.9500
As1—C1	1.898 (12)	C6—H6	0.9500
O1W—H11W	0.89 (9)		
O1W—Cs1—O2W	76.6 (2)	Cs1—O1W—Cs1^{vii}	83.2 (2)
O1W—Cs1—O11	85.6 (2)	Cs1—O2W—Cs2^{viii}	169.7 (4)
O1W—Cs1—O1W^{i}	158.4 (2)	Cs1—O2W—Cs1^{vii}	81.9 (3)
O1W—Cs1—O2W^{i}	86.2 (2)	Cs1^{vii}—O2W—Cs2^{viii}	87.8 (3)
O1W—Cs1—O1W^{ii}	96.7 (2)	Cs1—O11—Cs2	91.7 (2)
O1W—Cs1—O11^{ii}	153.0 (2)	Cs1—O11—As1	131.1 (4)
O1W—Cs1—O1W^{iii}	85.1 (2)	Cs2—O11—As1	111.9 (4)
O2W—Cs1—O11	77.8 (2)	Cs2^{ix}—O12—As1	118.2 (4)
O1W^{i}—Cs1—O2W	124.49 (19)	Cs1^{vii}—O1W—H12W	58 (7)
O2W—Cs1—O2W^{i}	153.9 (3)	Cs1—O1W—H12W	123 (7)
O1W^{ii}—Cs1—O2W	76.6 (2)	H11W—O1W—H12W	91 (11)
O2W—Cs1—O11^{ii}	77.8 (2)	Cs1—O1W—H11W	142 (8)
O1W^{iii}—Cs1—O2W	124.49 (19)	Cs1^{vii}—O1W—H11W	103 (8)
O1W^{i}—Cs1—O11	102.5 (2)	Cs1—O2W—H21W^{ii}	59 (8)
O2W^{i}—Cs1—O11	120.8 (2)	Cs2^{viii}—O2W—H21W	124 (7)
O1W^{ii}—Cs1—O11	153.0 (2)	Cs1—O2W—H21W	59 (8)
O11—Cs1—O11^{ii}	80.8 (2)	H21W—O2W—H21W^{ii}	107 (11)
O1W^{iii}—Cs1—O11	48.5 (2)	Cs2^{viii}—O2W—H21W^{ii}	124 (8)
O1W^{i}—Cs1—O2W^{i}	72.4 (2)	Cs1^{vii}—O2W—H21W	103 (8)
O1W^{i}—Cs1—O1W^{ii}	85.1 (2)	Cs1^{vii}—O2W—H21W^{ii}	103 (9)
O1W^{i}—Cs1—O11^{ii}	48.5 (2)	Cs2^{ix}—O12—H12	121 (11)
O1W^{i}—Cs1—O1W^{iii}	85.5 (2)	As1—O12—H12	101 (10)

O1W^{ii}—Cs1—O2W^{i}	86.2 (2)	C4—N4—H41	103 (10)
O2W^{i}—Cs1—O11^{ii}	120.8 (2)	C4—N4—H42	119 (8)
O1W^{iii}—Cs1—O2W^{i}	72.4 (2)	H41—N4—H42	122 (13)
O1W^{ii}—Cs1—O11^{ii}	85.6 (2)	C2—C1—C6	119.3 (11)
O1W^{ii}—Cs1—O1W^{iii}	158.4 (2)	As1—C1—C2	119.3 (8)
O1W^{iii}—Cs1—O11^{ii}	102.5 (2)	As1—C1—C6	121.3 (8)
O2W^{iv}—Cs2—O11	114.3 (2)	C1—C2—C3	120.1 (11)
O11—Cs2—O12^{v}	175.8 (2)	C2—C3—C4	121.9 (11)
O11—Cs2—O11^{ii}	81.3 (2)	N4—C4—C5	118.3 (10)
O11—Cs2—O12^{vi}	94.9 (2)	N4—C4—C3	123.6 (10)
O2W^{iv}—Cs2—O12^{v}	68.7 (2)	C3—C4—C5	118.2 (11)
O2W^{iv}—Cs2—O11^{ii}	114.3 (2)	C4—C5—C6	119.9 (11)
O2W^{iv}—Cs2—O12^{vi}	68.7 (2)	C1—C6—C5	120.5 (10)
O11^{ii}—Cs2—O12^{v}	94.9 (2)	C1—C2—H2	120.00
O12^{v}—Cs2—O12^{vi}	88.9 (3)	C3—C2—H2	120.00
O11^{ii}—Cs2—O12^{vi}	175.8 (2)	C2—C3—H3	119.00
O11—As1—O12	109.3 (4)	C4—C3—H3	119.00
O11—As1—O13	112.3 (4)	C4—C5—H5	120.00
O11—As1—C1	111.5 (4)	C6—C5—H5	120.00
O12—As1—O13	103.1 (4)	C1—C6—H6	120.00
O12—As1—C1	107.3 (4)	C5—C6—H6	120.00
O13—As1—C1	112.8 (4)		

O11—Cs1—O1W—Cs1^{vii}	126.4 (2)	O13—As1—O11—Cs1	3.5 (6)
O1W—Cs1—O11—Cs2	175.0 (2)	O13—As1—O11—Cs2	116.5 (4)
O1W—Cs1—O11—As1	−63.7 (5)	C1—As1—O11—Cs1	131.1 (5)
O2W—Cs1—O11—Cs2	−107.8 (2)	C1—As1—O11—Cs2	−115.8 (4)
O2W—Cs1—O11—As1	13.5 (5)	O11—As1—O12—Cs2^{ix}	98.9 (5)
O1W^{i}—Cs1—O11—Cs2	15.3 (3)	O13—As1—O12—Cs2^{ix}	−20.8 (5)
O1W^{i}—Cs1—O11—As1	136.6 (5)	C1—As1—O12—Cs2^{ix}	−140.0 (5)
O2W^{i}—Cs1—O11—As1	−146.6 (5)	O11—As1—C1—C2	−4.7 (10)
O1W^{ii}—Cs1—O11—Cs2	−88.9 (5)	O11—As1—C1—C6	178.4 (8)
O1W^{ii}—Cs1—O11—As1	32.4 (9)	O12—As1—C1—C2	−124.4 (8)
O11^{ii}—Cs1—O11—Cs2	−28.4 (2)	O12—As1—C1—C6	58.7 (9)
O11^{ii}—Cs1—O11—As1	93.0 (5)	O13—As1—C1—C2	122.7 (8)
O1W^{iii}—Cs1—O11—Cs2	87.6 (3)	O13—As1—C1—C6	−54.2 (9)
O1W^{iii}—Cs1—O11—As1	−151.1 (6)	As1—C1—C2—C3	−177.4 (9)
O1W—Cs1—O11^{ii}—Cs2	88.9 (5)	C6—C1—C2—C3	−0.5 (16)
O11—Cs1—O11^{ii}—Cs2	28.4 (2)	As1—C1—C6—C5	176.9 (9)
O2W^{iv}—Cs2—O11—As1	139.6 (4)	C2—C1—C6—C5	0.0 (16)
O11^{ii}—Cs2—O11—Cs1	28.5 (2)	C1—C2—C3—C4	2.2 (18)
O11^{ii}—Cs2—O11—As1	−107.6 (4)	C2—C3—C4—N4	178.1 (11)
O12^{vi}—Cs2—O11—Cs1	−153.2 (2)	C2—C3—C4—C5	−3.4 (18)
O12^{vi}—Cs2—O11—As1	70.7 (4)	N4—C4—C5—C6	−178.5 (11)
O11—Cs2—O11^{ii}—Cs1	−28.5 (2)	C3—C4—C5—C6	2.9 (18)

O12—As1—O11—Cs1	−110.3 (5)	C4—C5—C6—C1	−1.2 (18)
O12—As1—O11—Cs2	2.7 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···N4$^{\mathrm{x}}$	0.89 (9)	2.28 (13)	2.952 (13)	132 (10)
O2*W*—H21*W*···O13	0.89 (12)	2.16 (12)	2.850 (10)	134 (12)
O12—H12···O13$^{\mathrm{vi}}$	0.88 (5)	2.00 (12)	2.567 (13)	121 (12)
N4—H41···O1*W*$^{\mathrm{xi}}$	0.83 (14)	2.12 (15)	2.928 (15)	164 (9)
N4—H42···O13$^{\mathrm{xii}}$	0.91 (14)	2.20 (14)	3.082 (13)	166 (15)

Symmetry codes: (vi) *x*, −*y*+1, *z*+1/2; (x) −*x*+3/2, −*y*+3/2, *z*−1/2; (xi) −*x*+3/2, *y*−1/2, *z*; (xii) −*x*+3/2, −*y*+3/2, *z*+1/2.