Syntheses and crystal structures of a new family of hybrid perovskites: $C_5H_{14}N_2 \cdot ABr_3 \cdot 0.5H_2O$ (A = K, Rb, Cs)

Sarah Ferrandin,[a] Alexandra M. Z. Slawin[b] and William T. A. Harrison[a]*

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, and [b]Department of Chemistry, University of St Andrews, KY16 9ST, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

The syntheses and crystal structures of three hybrid perovskites, *viz.* poly[1-methylpiperizine-1,4-diium [tri-μ-bromido-potassium] hemihydrate], $\{(C_5H_{14}N_2)[KBr_3] \cdot 0.5H_2O\}_n$, (I), poly[1-methylpiperizine-1,4-diium [tri-μ-bromido-rubidium] hemihydrate], $\{(C_5H_{14}N_2)[RbBr_3] \cdot 0.5H_2O\}_n$, (II), and poly[1-methyl-piperizine-1,4-diium [tri-μ-bromido-caesium] hemihydrate], $\{(C_5H_{14}N_2)-[CsBr_3] \cdot 0.5H_2O\}_n$, (III), are described. These isostructural (space group $Amm2$) phases contain a three-dimensional, corner-sharing network of distorted ABr_6 octahedra (A = K, Rb, Cs) with the same topology as the classical perovskite structure. The doubly protonated $C_5H_{14}N_2^{2+}$ cations occupy interstices bounded by eight octahedra and the water molecules lie in square sites bounded by four octahedra. N—H$\cdots$Br, N—H$\cdots$(Br,Br), N—H$\cdots$O and O—H$\cdots$Br hydrogen bonds consolidate the structures.

1. Chemical context

Oxide perovskites of generic formula ABO_3, where A and B are metal ions with a combined charge of +6, are probably the most-studied family of inorganic phases on account of their numerous physical properties and structural variety (Tilley, 2016). The aristotype (highest-possible symmetry) (Megaw, 1973) for this classic structure type is a three-dimensional network (space group $Pm\overline{3}m$) of undistorted, vertex-sharing, BO_6 octahedra encapsulating the A cations in 12-coordinate dodecahedral cavities bounded by eight octahedra but lower symmetry ('hettotype') structures are very common, which can be systematically described in terms of tilting schemes of the octahedra (Woodward, 1997).

'Hybrid' RMX_3 perovskites containing both inorganic and organic (molecular) components have been studied intensively in the last few years due to their remarkable photovoltaic and other optical properties (Xu *et al.*, 2019; Stylianakis *et al.*, 2019; Zuo *et al.*, 2019). The R^+ or R^{2+} organic cation replaces the metallic A cation in an oxide perovskite and the MX_3 (X = halide) octahedral network replaces the BO_3 component of an oxide perovskite. Many of these studies have focused on lead halides [there are over 1400 papers on $CH_3NH_3PbX_3$ (X = Br, I) alone as of July 2019] and tin halides as the inorganic component of the structure (Stoumpos *et al.*, 2016) but other compositions are possible: several years ago, we described a family of alkali-metal–chloride perovskites templated by $C_4H_{12}N_2^{2+}$ piperizinium (or piperazin-1,4-diium) or $C_6H_{14}N_2^{2+}$ 'dabconium' (or 1,4-diazoniabicyclo[2.2.2]octane) cations (Paton & Harrison, 2010). Notable features of these structures include the 'inverse' charges of the cations ($R^{2+} > M^+$) compared to oxide perovskites, the inclusion of
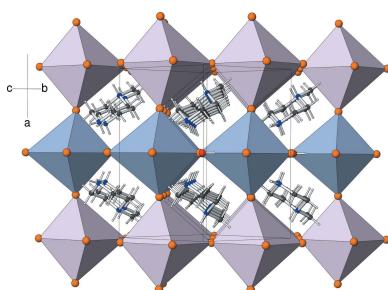
water molecules of hydration in the $C_4H_{12}N_2 \cdot ACl_3 \cdot H_2O$ (A = K, Rb, Cs) series and a novel chiral perovskite analogue (space group $P3_221$) for $C_6H_{14}N_2 \cdot RbCl_3$. This family has recently been extended by a number of phases (see *Database survey*) including $C_6H_{14}N_2 \cdot RbBr_3$ and $C_7H_{16}N_2 \cdot RbI_3$ ($C_7H_{16}N_2{}^{2+}$ = 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium) (Zhang *et al.*, 2017), $C_4H_{12}N_2 \cdot RbBr_3$ ($C_4H_{12}N_2{}^{2+}$ = 3-ammoniopyrrolidinium) (Pan *et al.*, 2017) and $C_4H_{12}N_2 \cdot NaI_3$ (Chen *et al.*, 2018), some of which have significant physical properties such as ferroelectricity.

(I) A = K

(II) A = Rb ABr_3 0.5 H_2O

(III) A = Cs
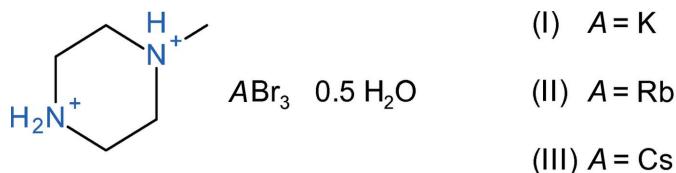
In this paper we describe the syntheses and structures of a new family of isostructural hybrid perovskite hemihydrates of formula $C_5H_{14}N_2 \cdot ABr_3 \cdot 0.5H_2O$ ($C_5H_{14}N_2{}^{2+}$ = 1-methyl piperizinium cation) where A = K (I), Rb (II) and Cs (III).

2. Structural commentary

Compounds (I), (II) and (III) are isostructural as indicated by their orthorhombic unit cells, showing the expected trend of volume increase as a result of the increasing ionic radius (Shannon, 1976) of the alkali-metal cation on going from potassium (r = 1.52) to rubidium (r = 1.66) to caesium (r = 1.81 Å). This description will focus on the structure of (I) and note significant differences for (II) and (III) where applicable.

The asymmetric unit of (I) (Fig. 1) contains two methylene groups (C1 and C2), an $N1H_2{}^+$ grouping, an $N2H^+$ moiety and
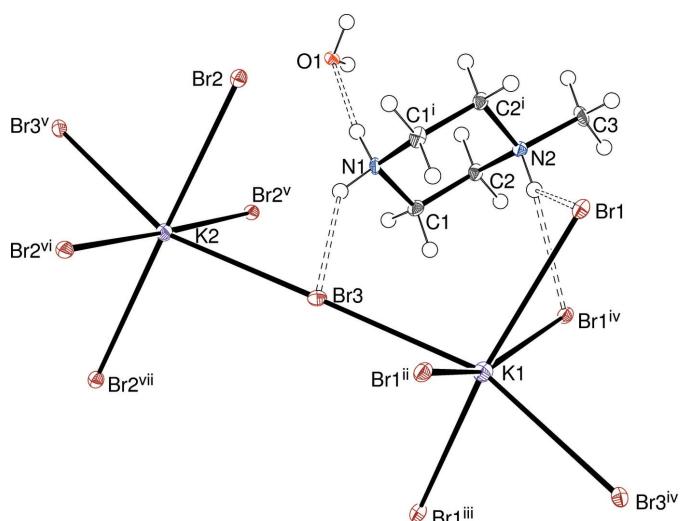

Figure 1
The asymmetric unit of (I) expanded to show the complete $C_5H_{14}N_2{}^{2+}$ cation, the complete potassium coordination polyhedra and the water molecule (50% displacement ellipsoids). Symmetry codes: (i) $x, 1 - y, z$; (ii) $2 - x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x, y - \frac{1}{2}, \frac{1}{2} + z$; (iv) $2 - x, 1 - y, z$; (v) $1 - x, 1 - y, z$; (vi) $1 - x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $x, y - \frac{1}{2}, \frac{1}{2} + z$.

Table 1
Selected geometric parameters (Å, °) for (I).

K1—Br1^i	3.4184 (13)	K2—Br2	3.4000 (16)
K1—Br1	3.5261 (18)	K2—Br2^{ii}	3.4179 (15)
K1—Br3	3.4865 (10)	K2—Br3	3.3297 (10)
K1^{iii}—Br1—K1	157.98 (5)	K2—Br3—K1	179.19 (5)
K2—Br2—K2^{iii}	177.85 (5)		

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

Table 2
Selected geometric parameters (Å, °) for (II).

Rb1—Br1^i	3.4639 (8)	Rb2—Br2	3.4326 (9)
Rb1—Br1	3.5323 (10)	Rb2—Br2^{ii}	3.4336 (9)
Rb1—Br3	3.4756 (9)	Rb2—Br3	3.3919 (9)
Rb1^{iii}—Br1—Rb1	157.67 (2)	Rb2—Br3—Rb1	178.12 (3)
Rb2—Br2—Rb2^{iii}	176.93 (2)		

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

Table 3
Selected geometric parameters (Å, °) for (III).

Cs1—Br1^i	3.5319 (9)	Cs2—Br2	3.4923 (10)
Cs1—Br1	3.5873 (10)	Cs2—Br2^{ii}	3.4790 (9)
Cs1—Br3	3.5105 (11)	Cs2—Br3	3.4627 (11)
Cs1^{iii}—Br1—Cs1	156.07 (2)	Cs2—Br3—Cs1	175.99 (3)
Cs2^{iii}—Br2—Cs2	174.97 (3)		

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

the carbon atom (C3) of a methyl group. N1, N2 and C3 lie on a (010) crystallographic mirror plane with $y = \frac{1}{2}$ for the asymmetric atoms. The complete $C_5H_{14}N_2{}^{2+}$ cation is generated by the mirror to result in a typical (Dennington & Weller, 2018) chair conformation for this species with N1 and N2 deviating from the C1/C2/C1^i/C2^i [symmetry code: (i) $x, 1 - y, z$] plane by -0.623 (7) and 0.708 (6) Å, respectively. The pendant C3 methyl group adopts an equatorial orientation with respect to the ring. A water molecule with the O atom lying on the $(\frac{1}{2}, \frac{1}{2}, z)$ special position with $mm2$ symmetry (Wyckoff site 2a) is also present.

The inorganic component of the structure consists of two potassium ions, K1 (site symmetry $mm2$; Wyckoff site 2b) and K2 ($mm2$; 2a) and three bromide ions: Br1 [$m(100)$; 4e], Br2 [$m(100)$; 4e] and Br3 [$m(010)$; 4c], which gives an overall inorganic stoichiometry of KBr_3. Crystal symmetry constructs Br_6 octahedra around each potassium ion and the mean K1—Br and K2—Br separations are 3.4770 and 3.3825 Å, respectively (Table 1); equivalent data for (II) (Table 2) are Rb1—Br = 3.4906 and Rb2—Br = 3.4194 Å; equivalent data for (III) (Table 3) are Cs1—Br = 3.5432 and Cs2—Br = 3.4780 Å. These data may be compared with the shortest K—Br and Rb—Br separations of 3.299 and 3.425 Å, respectively in the rocksalt-type KBr and RbBr structures and the Cs—Br separation of 3.716 Å in CsBr (eight-coordinate CsCl structure).

The K1 octahedron in (I) is considerably distorted with the smallest and largest *cis* Br—K—Br angles being 66.53 (4) and

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$N\cdots$O1	0.91	1.89	2.799 (5)	172
N1—H1$N\cdots$Br3	0.91	2.47	3.232 (5)	141
N2—H3$N\cdots$Br1	1.00	2.67	3.438 (4)	133
N2—H3$N\cdots$Br1^{iv}	1.00	2.67	3.438 (4)	133
O1—H1$O\cdots$Br2^v	0.87	2.34	3.200 (3)	172
C1—H1$A\cdots$Br2^{vi}	0.99	2.88	3.614 (4)	131
C1—H1$B\cdots$Br1^{iv}	0.99	3.00	3.703 (4)	129
C2—H2$B\cdots$Br1^{iv}	0.99	3.05	3.517 (4)	111
C2—H2$B\cdots$Br3^v	0.99	2.82	3.525 (4)	129
C3—H3$A\cdots$Br1^{vii}	0.98	2.96	3.857 (4)	153
C3—H3$B\cdots$Br3^{viii}	0.98	2.75	3.615 (6)	148

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$N\cdots$O1	0.91	1.91	2.816 (5)	173
N1—H2$N\cdots$Br3	0.91	2.49	3.243 (4)	140
N2—H3$N\cdots$Br1	1.00	2.68	3.448 (4)	134
N2—H3$N\cdots$Br1^{iv}	1.00	2.68	3.448 (4)	134
O1—H1$O\cdots$Br2^v	0.87	2.34	3.212 (3)	173
C1—H1$A\cdots$Br1^{iv}	0.99	3.01	3.717 (4)	129
C1—H1$B\cdots$Br2^{vi}	0.99	2.92	3.652 (4)	131
C2—H2$B\cdots$Br1^{iv}	0.99	3.06	3.531 (4)	111
C2—H2$B\cdots$Br3^v	0.99	2.85	3.560 (4)	130
C3—H3$A\cdots$Br1^{vii}	0.99	3.03	3.927 (4)	152
C3—H3$B\cdots$Br3^{viii}	0.99	2.79	3.653 (5)	146

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$N\cdots$O1	0.91	1.94	2.845 (7)	173
N1—H1$N\cdots$Br3	0.91	2.51	3.259 (6)	140
N2—H3$N\cdots$Br1	1.00	2.68	3.446 (5)	134
N2—H3$N\cdots$Br1^{iv}	1.00	2.68	3.446 (5)	134
O1—H1$O\cdots$Br2^v	0.89	2.36	3.242 (4)	175
C1—H1$A\cdots$Br1^{iv}	0.99	3.07	3.762 (5)	128
C1—H1$B\cdots$Br2^{vi}	0.99	2.99	3.712 (5)	131
C2—H2$B\cdots$Br1^{iv}	0.99	3.08	3.550 (5)	111
C2—H2$B\cdots$Br3^v	0.99	2.92	3.643 (4)	131
C3—H3$B\cdots$Br3^{vii}	1.00	2.86	3.726 (7)	145

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

110.57 (6)°, respectively and the *trans* angles spanning the range 157.98 (5)–160.13 (7)°. The K2 octahedron is more regular, with *cis* angles varying from 82.17 (3) to 97.55 (2)°. Two of the *trans* angles for K2 are close to 180° but the other is much smaller at 158.51 (7)°. The octahedral volume for the K1 octahedron is 53.2 Å^3 and its angular variance (Robinson *et al.*, 1971) is 125.5°^{2}. The equivalent data for the K2 octahedron are 50.7 Å^3 and 45.0°^{2}, respectively. The corresponding polyhedra in (II) and (III) are similarly distorted, with respective octahedral volumes and angular variances as follows: Rb1 53.7 Å^3, 129.7°^{2}; Rb2 52.1 Å^3, 56.6°^{2}; Cs1 55.8 Å^3, 145.2°^{2}; Cs2 54.2 Å^3, 84.7°^{2}.

Bond-valence-sum (BVS) calculations using the 'extrapolated' formalism of Brese & O'Keeffe (1991) give the following values in valence units: K1 0.66, K2 0.86, Rb1 0.88 Rb2 1.07, Cs1 1.21, Cs2 1.44 (expected value = 1.00 in all cases). These data suggest that K1 in (I) is considerably underbonded, which is consistent with the long mean K1—Br separation in (I) compared to the separation in KBr. Conversely, Cs2 in (III) is substantially overbonded and must be a 'tight fit' in its octahedral site.
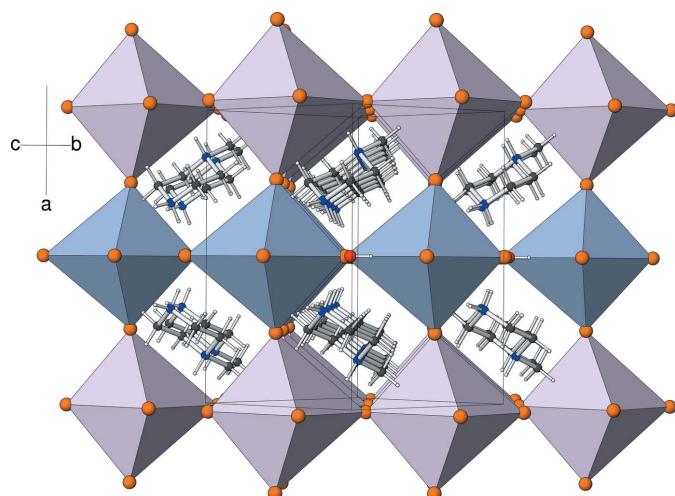

Figure 2
Polyhedral plot of the extended structure of (I) viewed down [011] with the K1Br$_6$ octahedra coloured lilac and K2Br$_6$ blue.

3. Supramolecular features

The linkage of the KBr$_6$ octahedra in (I) in the x, y and z directions through their bromide-ion vertices leads to an infinite network of corner-sharing KBr$_6$ octahedra akin to the network of BO$_6$ octahedra in the classical ABO_3 perovskite structure. Key features of the inorganic network are the K—Br—K bond angles (Table 1), with Br1 substantially bent from the nominal linear bond [K1—Br1—K1^{ii} = 157.98 (5)°; symmetry code (ii) $x, \frac{1}{2} + y, z - \frac{1}{2}$], but Br2 and Br3 far less so. When the structure of (I) is viewed down [011], alternating (100) layers of K1- and K2-centred octahedra are apparent (Fig. 2). Within these (100) planes, the K1 atoms are linked by the Br1 ions and the K2 atoms are liked by the Br2 ions. Finally, Br3 provides the inter-layer linkages in the [100] direction.

The 1-methylpiperizinium cations occupy the central regions of the cages formed by eight KBr$_6$ octahedra, obviously equivalent to the A cation site in a classical perovskite. The water molecules lie at the centres of square sites bounded by four octahedra and stack in the [100] direction with alternating occupied and empty sites (see Fig. 3 and the *Database survey* section). Hydrogen bonding involving the encapsulated species is an important feature of the structure of (I): the N1H$_2^+$ group forms one N—H$\cdots$Br3 link and one N—H$\cdots$O link to the water molecule (Table 4, Fig. 1) whereas the methylated N2H$^+$ group forms a rather long (and presumably weak) bifurcated N—H$\cdots$(Br1,Br1) link. As just

Code/refcode	Formula	Space group	Reference
(I)	$C_5H_{14}N_2 \cdot KBr_3 \cdot 0.5H_2O$	$Amm2$	This work
(II)	$C_5H_{14}N_2 \cdot RbBr_3 \cdot 0.5H_2O$	$Amm2$	This work
(III)	$C_5H_{14}N_2 \cdot CsBr_3 \cdot 0.5H_2O$	$Amm2$	This work
GUYMIX	$C_4H_{12}N_2 \cdot KCl_3 \cdot H_2O$	$Pbcm$	Paton & Harrison (2010)
GUYMOD	$C_4H_{12}N_2 \cdot RbCl_3 \cdot H_2O$	$Pbcm$	Paton & Harrison (2010)
GUYMUJ	$C_4H_{12}N_2 \cdot CsCl_3 \cdot H_2O$	$Pbcm$	Paton & Harrison (2010)
MOMLEI	$C_4H_{12}N_2 \cdot KBr_3 \cdot H_2O$	$Pbcm$	Harrison (2019a)
MOMSEP	$C_4H_{12}N_2 \cdot RbBr_3 \cdot H_2O$	$Pbcm$	Harrison (2019b)
FIZYIZ	$C_6H_{14}N_2 \cdot KBr_3$	$P3_121$	Hongzhang (2019)
GUYNEU	$C_6H_{14}N_2 \cdot RbCl_3$	$P3_221$	Paton & Harrison (2010)
HEJGUB	$C_6H_{14}N_2 \cdot RbBr_3$	$P3_221$	Zhang et al. (2017)
GUYNEU02[a]	$C_6H_{14}N_2 \cdot RbCl_3$	$Pm\overline{3}m$	Zhang et al. (2017)
HEJGUB01[a]	$C_6H_{14}N_2 \cdot RbBr_3$	$Pm\overline{3}m$	Zhang et al. (2017)
GUYNIY	$C_6H_{14}N_2 \cdot CsCl_3$	$C2/c$	Paton & Harrison (2010)
HEJGOV	$C_7H_{16}N_2 \cdot RbI_3$	$P432$	Zhang et al. (2017)
HEJGOV01	$C_7H_{16}N_2 \cdot RbI_3$	$R3$	Zhang et al. (2017)
GEFLOV	$C_4H_{12}N_2 \cdot RbBr_3$	Ia	Pan et al. (2017)
GEFLOV01[a]	$C_4H_{12}N_2 \cdot RbBr_3$	$Pm\overline{3}m$	Pan et al. (2017)
MEXMAG	$C_4H_{12}N_2 \cdot NaI_3$	$C2/c$	Chen et al. (2018)

Redetermined structures not included. Note: (a) high-temperature polymorph.

noted, the water molecule accepts an N—H⋯O hydrogen bond from the organic cation and forms a pair of symmetry-equivalent O—H⋯Br2 hydrogen bonds. It is notable that *all* the C-bound H atoms in (I) are also potential hydrogen-bond donors to bromide ions based on the H⋯Br separations being significantly less than the van der Waals' separation of 3.05 Å for these atoms. So far as the bromide ions are concerned, Br1 accepts one classical and three non-classical hydrogen bonds, Br2 accepts one classical and one non-classical and Br3 accepts one classical and two non-classical. The hydrogen-bonding schemes for (II) (Table 5) and (III) (Table 6) are essentially the same as that for (I).

4. Database survey

The title compounds and their significant analogue structures with their space groups and CCDC refcodes (Groom et al., 2016) are listed in Table 7. These compounds now represent a significant family of hybrid perovskites featuring several different cations – the protonated forms of piperazine, dabco, 1-methylpiperazine, 3-aminopyrrolidine and 'methyl dabco' (1-methyl-1,4-diazabicyclo[2.2.2]octane) – as well as different alkali metal cations and halide anions. The recently reported structure of MEXMAG (Chen et al., 2108) has added sodium to the list of cations that can form these structures. Some structures such as HEJGOV (Zhang et al., 2017) show notable
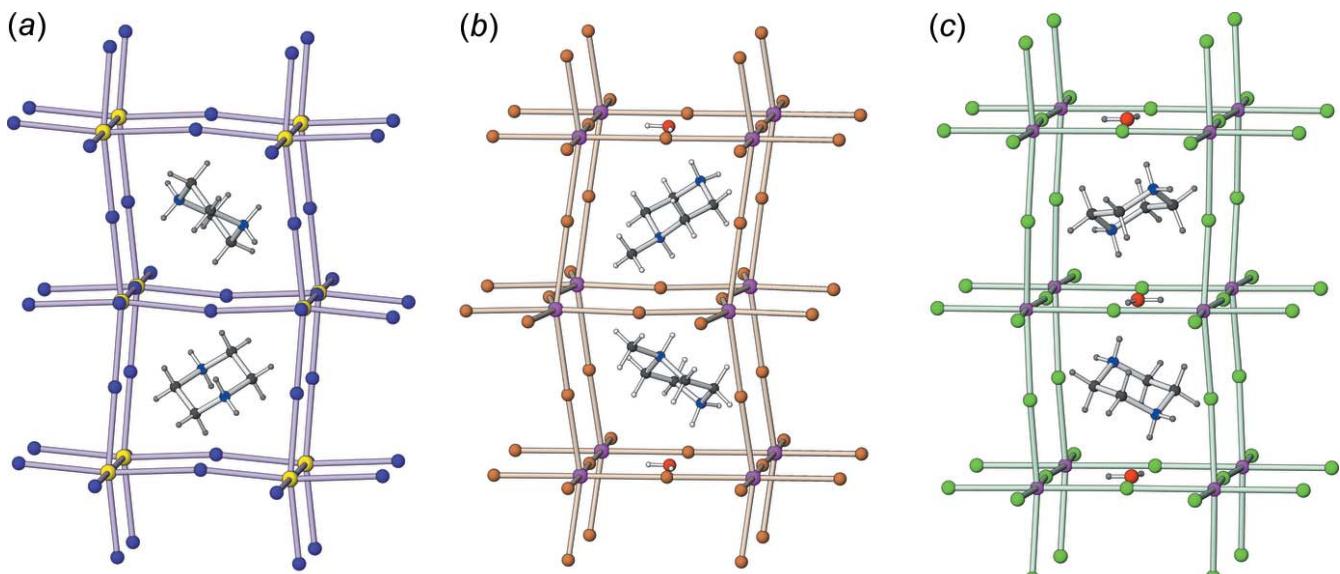
Figure 3
Comparison of the structures of (a) MEXMAG (redrawn from Chen et al., 2018), (b) (I) and (c) GUYMIX (redrawn from Paton and Harrison, 2010). In MEXMAG, (I) and GUYMIX, the two octahedral cages shown are stacked in the [001], [100] and [001] directions, respectively. Note the alternation of water molecules and empty sites in (I) with respect to the [100] direction whereas GUYMIX has a water molecule in every square site in the [001] direction.

Table 8
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$(C_5H_{14}N_2)[KBr_3]\cdot0.5H_2O$	$(C_5H_{14}N_2)[RbBr_3]\cdot0.5H_2O$	$(C_5H_{14}N_2)[CsBr_3]\cdot0.5H_2O$
M_r	390.02	436.39	483.83
Crystal system, space group	Orthorhombic, $Amm2$	Orthorhombic, $Amm2$	Orthorhombic, $Amm2$
Temperature (K)	93	93	93
a, b, c (Å)	13.411 (3), 9.488 (2), 9.790 (2)	13.477 (3), 9.5617 (19), 9.850 (2)	13.610 (3), 9.7201 (19), 9.977 (2)
V (Å^3)	1245.7 (5)	1269.3 (5)	1319.9 (5)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	10.01	13.31	11.85
Crystal size (mm)	$0.10 \times 0.08 \times 0.08$	$0.15 \times 0.10 \times 0.10$	$0.10 \times 0.10 \times 0.10$
Data collection			
Diffractometer	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)
T_{min}, T_{max}	0.406, 1.000	0.347, 1.000	0.463, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3890, 1235, 1208	6851, 1264, 1244	3718, 1312, 1293
R_{int}	0.033	0.037	0.022
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.602	0.603
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.031, 0.90	0.013, 0.028, 1.01	0.013, 0.029, 0.94
No. of reflections	1235	1264	1312
No. of parameters	68	69	68
No. of restraints	1	1	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.41, −0.36	0.27, −0.35	0.58, −0.70
Absolute structure	Parsons *et al.* (2013)	Parsons *et al.* (2013)	Parsons *et al.* (2013)
Absolute structure parameter	−0.001 (11)	−0.001 (13)	0.016 (7)

Computer programs: *CrysAlis PRO* (Rigaku, 2017), *SHELXS7* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

physical properties such as ferroelectricity, which is of course a classic characteristic of oxide perovskites.

An interesting structural comparison may be made between MEXMAG (an 'anhydrous' RAX_3 hybrid perovskite), (I) (an $RAX_3\cdot0.5H_2O$ hybrid perovskite hemihydrate) and GUYMIX (an $RAX_3\cdot H_2O$ hybrid perovskite hydrate) (Fig. 3). It may be seen that the pendant methyl groups of the $C_5H_{14}N_2{}^{2+}$ cations in (I) both point towards an empty square site and their steric bulk presumably prevents water molecules from occupying that site. It is notable that the empty square site in (I) is associated with the reduced K1—Br1—K1 bond angles as noted above. Conversely, in MEXMAG, the iodide ions are perhaps too large to allow a water molecule to fit between them and the piperazinium cation is forced to form long N—H⋯I hydrogen bonds (H⋯I = 3.14 Å) rather than N—H⋯O$_w$ (w = water) links.

5. Synthesis and crystallization

To prepare (I), 0.3673 g (3.67 mmol) of 1-methyl piperazine and 0.4068 g (3.42 mmol) of KBr were added to 15.0 ml of 1.0 *M* aqueous HBr solution to result in a clear solution, which was left in a Petri dish to evaporate. After two or three days, colourless blocks of (I) were recovered, rinsed with acetone and dried in air. Compound (II) was prepared in the same way, with 0.4042 g (2.44 mmol) of RbBr replacing the KBr in (I)

and (III) was prepared by using 0.4479 g (2.10 mmol) of CsBr in place of the KBr.

ATR–FTIR (cm^{-1}) for (I) (selected): 3215*m* (NH$_2$ asymmetric stretch), 2940*s* (NH$_2$ symmetric stretch), 2692*s* (sp^3 C—H stretch), 1585*s* (NH$_2$ bend) (assignments from Heacock & Marion, 1956); for (II) 3217*s*, 2998*s*, 2681*s*, 1548*s*; for (III) 3221*m*, 2995*s*, 2681*s*, 1548*s*. The IR spectra of (I), (II) and (III) are available in the supporting information.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 8. For each structure, the N- and C-bond hydrogen atoms were located geometrically (C—H = 0.98–0.99, N—H = 0.91–1.00Å) and refined as riding atoms. The water H atom was located in a difference map and refined as riding in its as-found relative position. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl C) was applied in all cases.

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Chen, X.-G., Gao, J.-X., Hua, X.-N. & Liao, W.-Q. (2018). *Acta Cryst.* C**74**, 728–733.
Dennington, A. J. & Weller, M. T. (2018). *Dalton Trans.* **47**, 3469–3484.

research communications

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.

Harrison, W. T. A. (2019*a*). Private communication (refcode MOMLEI). CCDC, Cambridge, England.

Harrison, W. T. A. (2019*b*). Private communication (refcode MOMSEP). CCDC, Cambridge, England.

Heacock, R. A. & Marion, L. (1956). *Can. J. Chem.* **34**, 1782–1795.

Hongzhang (2019). Private communication (refcode FIZYIZ). CCDC, Cambridge, England.

Megaw, H. D. (1973). *Crystal Structures: a Working Approach*. Philadelphia: Saunders.

Pan, Q., Liu, Z. B., Tang, Y. Y., Li, P. F., Ma, R. W., Wei, R. Y., Zhang, Y., You, Y. M., Ye, H. Y. & Xiong, R. G. (2017). *J. Am. Chem. Soc.* **139**, 3954–3957.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Paton, L. A. & Harrison, W. T. (2010). *Angew. Chem. Int. Ed.* **49**, 7684–7687.

Rigaku (2017). *CrysAlis PRO*. Rigaku Corporation, Tokyo, Japan.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

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

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Stoumpos, C. C., Cao, D. H., Clark, D. J., Young, J., Rondinelli, J. M., Jang, J. I., Hupp, J. T. & Kanatzidis, M. G. (2016). *Chem. Mater.* **28**, 2852–2867.

Stylianakis, M. M., Maksuov, T., Panagiotopoulos, A., Kakavelakis, G. & Petridis, K. (2019). *Materials*, 12, article 859 (28 pages).

Tilley, R. J. D. (2016). *Perovskites: Structure–Property Relationships*. New York: Wiley.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Woodward, P. M. (1997). *Acta Cryst.* B**53**, 32–43.

Xu, W.-J., Kopyl, S., Kholkin, A. & Rocha, J. (2019). *Coord. Chem. Rev.* **387**, 398–414.

Zhang, W. Y., Tang, Y. Y., Li, P. F., Shi, P. P., Liao, W. Q., Fu, D. W., Ye, H. Y., Zhang, Y. & Xiong, R. G. (2017). *J. Am. Chem. Soc.* **139**, 10897–10902.

Zuo, T. T., He, X. X., Hu, P. & Jiang, H. (2019). *Chemnanomat*, **5**, 278–289.

supporting information

Syntheses and crystal structures of a new family of hybrid perovskites: $C_5H_{14}N_2$·ABr_3·$0.5H_2O$ (*A* = K, Rb, Cs)

Sarah Ferrandin, Alexandra M. Z. Slawin and William T. A. Harrison

Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku, 2017); cell refinement: *CrysAlis PRO* (Rigaku, 2017); data reduction: *CrysAlis PRO* (Rigaku, 2017); program(s) used to solve structure: *SHELXS7* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[1-methylpiperizine-1,4-diium [tri-*μ*-bromido-potassium] hemihydrate] (I)

Crystal data

$(C_5H_{14}N_2)[KBr_3]$·$0.5H_2O$	$D_x = 2.080$ Mg m^{-3}
$M_r = 390.02$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Amm2$	Cell parameters from 2257 reflections
$a = 13.411$ (3) Å	$\theta = 3.0–27.2°$
$b = 9.488$ (2) Å	$\mu = 10.01$ mm^{-1}
$c = 9.790$ (2) Å	$T = 93$ K
$V = 1245.7$ (5) Å^3	Prism, colourless
$Z = 4$	$0.10 \times 0.08 \times 0.08$ mm
$F(000) = 748$	

Data collection

Rigaku Pilatus 200K CCD diffractometer	1235 independent reflections
	1208 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan (CrysalisPro; Rigaku, 2017)	$\theta_{max} = 25.3°$, $\theta_{min} = 3.0°$
$T_{min} = 0.406$, $T_{max} = 1.000$	$h = -16\rightarrow16$
	$k = -11\rightarrow11$
3890 measured reflections	$l = -11\rightarrow11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.015$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.031$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
$S = 0.90$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
1235 reflections	Extinction correction: SHELXL-2014/7
68 parameters	(Sheldrick 2015),
1 restraint	$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00195 (16)
	Absolute structure: Parsons *et al.* (2013)
Hydrogen site location: mixed	Absolute structure parameter: −0.001 (11)
H-atom parameters constrained	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
K1	1.0000	0.5000	0.9058 (2)	0.0145 (4)
K2	0.5000	0.5000	1.0306 (2)	0.0120 (3)
Br1	1.0000	0.70384 (5)	0.60463 (6)	0.01165 (14)
Br2	0.5000	0.74449 (6)	0.77675 (6)	0.01087 (14)
Br3	0.74393 (4)	0.5000	0.96724 (6)	0.01101 (14)
C1	0.7289 (3)	0.3693 (4)	0.6163 (5)	0.0123 (9)
H1A	0.6861	0.2859	0.6321	0.015*
H1B	0.7878	0.3614	0.6767	0.015*
C2	0.7626 (3)	0.3706 (4)	0.4700 (5)	0.0107 (8)
H2A	0.7038	0.3696	0.4089	0.013*
H2B	0.8027	0.2851	0.4510	0.013*
C3	0.8629 (4)	0.5000	0.2985 (6)	0.0145 (12)
H3A	0.9028	0.5851	0.2831	0.022*
H3B	0.8067	0.5000	0.2346	0.022*
N1	0.6720 (3)	0.5000	0.6522 (5)	0.0098 (10)
H1N	0.6586	0.5000	0.7433	0.012*
H2N	0.6128	0.5000	0.6067	0.012*
N2	0.8244 (3)	0.5000	0.4421 (5)	0.0091 (10)
H3N	0.8827	0.5000	0.5059	0.011*
O1	0.5000	0.5000	0.4902 (5)	0.0088 (12)
H1O	0.5000	0.4251	0.4392	0.011*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0132 (9)	0.0147 (8)	0.0156 (10)	0.000	0.000	0.000
K2	0.0105 (8)	0.0138 (8)	0.0117 (9)	0.000	0.000	0.000
Br1	0.0086 (3)	0.0111 (3)	0.0152 (3)	0.000	0.000	−0.0018 (2)
Br2	0.0102 (3)	0.0114 (3)	0.0110 (3)	0.000	0.000	−0.0015 (2)
Br3	0.0119 (3)	0.0102 (3)	0.0110 (3)	0.000	−0.0026 (2)	0.000
C1	0.0105 (17)	0.0092 (18)	0.017 (2)	0.0022 (14)	0.0017 (18)	0.0032 (19)
C2	0.0098 (18)	0.0087 (17)	0.014 (2)	−0.0005 (14)	0.0021 (19)	0.000 (2)
C3	0.017 (3)	0.019 (3)	0.008 (3)	0.000	0.005 (3)	0.000
N1	0.007 (2)	0.014 (2)	0.008 (3)	0.000	0.0026 (19)	0.000
N2	0.009 (2)	0.009 (2)	0.010 (3)	0.000	0.0003 (19)	0.000
O1	0.012 (2)	0.008 (2)	0.007 (3)	0.000	0.000	0.000

Geometric parameters (Å, º)

K1—Br1[i]	3.4184 (13)	C1—C2	1.502 (6)
K1—Br1[ii]	3.4184 (13)	C1—H1A	0.9900
K1—Br1[iii]	3.5261 (18)	C1—H1B	0.9900
K1—Br1	3.5261 (18)	C2—N2	1.506 (4)
K1—Br3	3.4865 (10)	C2—H2A	0.9900
K1—Br3[iii]	3.4865 (10)	C2—H2B	0.9900
K2—Br2[iv]	3.4000 (16)	C3—N2	1.497 (7)
K2—Br2	3.4000 (16)	C3—H3A	0.9800
K2—Br2[v]	3.4179 (15)	C3—H3B	0.9799
K2—Br2[ii]	3.4179 (15)	N1—C1[vii]	1.498 (4)
K2—Br3[iv]	3.3297 (10)	N1—H1N	0.9100
K2—Br3	3.3297 (10)	N1—H2N	0.9100
Br1—K1[vi]	3.4183 (13)	N2—C2[vii]	1.506 (4)
Br2—K2[vi]	3.4179 (15)	N2—H3N	1.0000
C1—N1	1.498 (4)	O1—H1O	0.8686
Br1[i]—K1—Br1[ii]	110.57 (6)	K1[vi]—Br1—K1	157.98 (5)
Br1[i]—K1—Br3	84.36 (2)	K2—Br2—K2[vi]	177.85 (5)
Br1[ii]—K1—Br3	84.36 (2)	K2—Br3—K1	179.19 (5)
Br1[i]—K1—Br3[iii]	84.36 (2)	N1—C1—C2	111.8 (3)
Br1[ii]—K1—Br3[iii]	84.36 (2)	N1—C1—H1A	109.3
Br3—K1—Br3[iii]	160.13 (7)	C2—C1—H1A	109.3
Br1[i]—K1—Br1[iii]	157.98 (5)	N1—C1—H1B	109.3
Br1[ii]—K1—Br1[iii]	91.449 (19)	C2—C1—H1B	109.3
Br3—K1—Br1[iii]	98.30 (3)	H1A—C1—H1B	107.9
Br3[iii]—K1—Br1[iii]	98.30 (3)	C1—C2—N2	110.2 (3)
Br1[i]—K1—Br1	91.449 (18)	C1—C2—H2A	109.6
Br1[ii]—K1—Br1	157.98 (5)	N2—C2—H2A	109.6
Br3—K1—Br1	98.30 (3)	C1—C2—H2B	109.6
Br3[iii]—K1—Br1	98.30 (3)	N2—C2—H2B	109.6
Br1[iii]—K1—Br1	66.53 (4)	H2A—C2—H2B	108.1
Br3[iv]—K2—Br3	158.51 (7)	N2—C3—H3A	109.4
Br3[iv]—K2—Br2[iv]	82.17 (3)	N2—C3—H3B	109.5
Br3—K2—Br2[iv]	82.17 (3)	H3A—C3—H3B	108.7
Br3[iv]—K2—Br2	82.17 (3)	C1—N1—C1[vii]	111.7 (4)
Br3—K2—Br2	82.17 (3)	C1—N1—H1N	109.3
Br2[iv]—K2—Br2	86.05 (5)	C1[vii]—N1—H1N	109.3
Br3[iv]—K2—Br2[v]	97.55 (2)	C1—N1—H2N	109.3
Br3—K2—Br2[v]	97.55 (2)	C1[vii]—N1—H2N	109.3
Br2[iv]—K2—Br2[v]	177.85 (5)	H1N—N1—H2N	107.9
Br2—K2—Br2[v]	91.800 (17)	C3—N2—C2[vii]	111.1 (3)
Br3[iv]—K2—Br2[ii]	97.55 (2)	C3—N2—C2	111.1 (3)
Br3—K2—Br2[ii]	97.55 (2)	C2[vii]—N2—C2	109.2 (4)
Br2[iv]—K2—Br2[ii]	91.800 (17)	C3—N2—H3N	108.4
Br2—K2—Br2[ii]	177.85 (5)	C2[vii]—N2—H3N	108.4
Br2[v]—K2—Br2[ii]	90.35 (5)	C2—N2—H3N	108.4

N1—C1—C2—N2	56.6 (4)	C1—C2—N2—C3	177.3 (3)
C2—C1—N1—C1ⁱⁱ	−52.9 (5)	C1—C2—N2—C2ⁱⁱ	−59.8 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2N···O1	0.91	1.89	2.799 (5)	172
N1—H1N···Br3	0.91	2.47	3.232 (5)	141
N2—H3N···Br1	1.00	2.67	3.438 (4)	133
N2—H3N···Br1ⁱⁱⁱ	1.00	2.67	3.438 (4)	133
O1—H1O···Br2ᵛⁱⁱⁱ	0.87	2.34	3.200 (3)	172
C1—H1A···Br2ⁱᵛ	0.99	2.88	3.614 (4)	131
C1—H1B···Br1ⁱⁱⁱ	0.99	3.00	3.703 (4)	129
C2—H2B···Br1ⁱⁱⁱ	0.99	3.05	3.517 (4)	111
C2—H2B···Br3ᵛⁱⁱⁱ	0.99	2.82	3.525 (4)	129
C3—H3A···Br1ⁱˣ	0.98	2.96	3.857 (4)	153
C3—H3B···Br3ˣ	0.98	2.75	3.615 (6)	148

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

Poly[1-methylpiperizine-1,4-diium [tri-μ-bromido-rubidium] hemihydrate] (II)

Crystal data

$(C_5H_{14}N_2)[RbBr_3]·0.5H_2O$	$D_x = 2.284$ Mg m⁻³
$M_r = 436.39$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Amm2$	Cell parameters from 2309 reflections
$a = 13.477$ (3) Å	$\theta = 3.0–27.4°$
$b = 9.5617$ (19) Å	$\mu = 13.31$ mm⁻¹
$c = 9.850$ (2) Å	$T = 93$ K
$V = 1269.3$ (5) Å³	Prism, colourless
$Z = 4$	$0.15 × 0.10 × 0.10$ mm
$F(000) = 820$	

Data collection

Rigaku Pilatus 200K CCD diffractometer	1264 independent reflections
	1244 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (CrysalisPro; Rigaku, 2017)	$\theta_{max} = 25.3°$, $\theta_{min} = 3.0°$
	$h = −16→16$
$T_{min} = 0.347$, $T_{max} = 1.000$	$k = −11→11$
6851 measured reflections	$l = −11→11$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.013$	
$wR(F^2) = 0.028$	Hydrogen site location: mixed
$S = 1.01$	H-atom parameters constrained
1264 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0076P)^2]$
69 parameters	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Extinction correction: SHELXL-2014/7
  (Sheldrick 2015),
  Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.00327 (14)
Absolute structure: Parsons *et al.* (2013)
Absolute structure parameter: −0.001 (13)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Rb1	0.0000	0.5000	0.09734 (7)	0.01032 (18)
Rb2	0.5000	0.5000	−0.03670 (8)	0.00968 (16)
Br1	0.0000	0.29829 (5)	0.39777 (6)	0.01090 (14)
Br2	0.5000	0.25694 (6)	0.21977 (6)	0.01073 (13)
Br3	0.25385 (4)	0.5000	0.03510 (6)	0.01017 (13)
C1	0.2708 (3)	0.6293 (4)	0.3838 (4)	0.0124 (8)
H1A	0.2118	0.6366	0.3243	0.015*
H1B	0.3130	0.7123	0.3674	0.015*
C2	0.2378 (3)	0.6284 (4)	0.5303 (5)	0.0117 (8)
H2A	0.2966	0.6293	0.5905	0.014*
H2B	0.1980	0.7131	0.5495	0.014*
C3	0.1383 (4)	0.5000	0.6996 (5)	0.0149 (12)
H3A	0.0985	0.4149	0.7150	0.022*
H3B	0.1945	0.5000	0.7635	0.022*
N1	0.3274 (3)	0.5000	0.3486 (5)	0.0107 (10)
H1N	0.3862	0.5000	0.3941	0.013*
H2N	0.3410	0.5000	0.2581	0.013*
N2	0.1766 (3)	0.5000	0.5584 (4)	0.0087 (9)
H3N	0.1187	0.5000	0.4950	0.010*
O1	0.5000	0.5000	0.5097 (5)	0.0109 (12)
H1O	0.5000	0.5749	0.5607	0.013*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0111 (4)	0.0093 (4)	0.0105 (4)	0.000	0.000	0.000
Rb2	0.0114 (4)	0.0091 (3)	0.0086 (3)	0.000	0.000	0.000
Br1	0.0122 (3)	0.0083 (3)	0.0122 (3)	0.000	0.000	0.0006 (2)
Br2	0.0141 (3)	0.0087 (3)	0.0094 (3)	0.000	0.000	0.0001 (2)
Br3	0.0112 (3)	0.0092 (3)	0.0101 (3)	0.000	−0.0012 (2)	0.000
C1	0.013 (2)	0.0077 (19)	0.017 (2)	−0.0003 (15)	−0.0003 (17)	0.0023 (18)
C2	0.013 (2)	0.0054 (18)	0.017 (2)	0.0009 (15)	0.0016 (18)	−0.001 (2)
C3	0.019 (3)	0.021 (3)	0.005 (3)	0.000	0.004 (2)	0.000
N1	0.011 (2)	0.012 (2)	0.009 (2)	0.000	0.0025 (19)	0.000

N2	0.009 (2)	0.010 (2)	0.007 (2)	0.000	−0.0010 (18)	0.000
O1	0.016 (3)	0.006 (2)	0.011 (3)	0.000	0.000	0.000

Geometric parameters (Å, º)

Rb1—Br1[i]	3.4639 (8)	C1—C2	1.510 (6)
Rb1—Br1[ii]	3.4639 (8)	C1—H1A	0.9900
Rb1—Br1[iii]	3.5323 (10)	C1—H1B	0.9900
Rb1—Br1	3.5323 (10)	C2—N2	1.504 (4)
Rb1—Br3[iii]	3.4756 (9)	C2—H2A	0.9900
Rb1—Br3	3.4756 (9)	C2—H2B	0.9900
Rb2—Br2[iv]	3.4326 (9)	C3—N2	1.484 (6)
Rb2—Br2	3.4326 (9)	C3—H3A	0.9868
Rb2—Br2[v]	3.4336 (9)	C3—H3B	0.9852
Rb2—Br2[ii]	3.4336 (9)	N1—C1[vii]	1.494 (4)
Rb2—Br3	3.3919 (9)	N1—H1N	0.9100
Rb2—Br3[iv]	3.3920 (9)	N1—H2N	0.9100
Br1—Rb1[vi]	3.4639 (8)	N2—C2[vii]	1.504 (4)
Br2—Rb2[vi]	3.4336 (9)	N2—H3N	1.0000
C1—N1	1.494 (4)	O1—H1O	0.8748
Br1[i]—Rb1—Br1[ii]	110.85 (3)	Rb1[vi]—Br1—Rb1	157.67 (2)
Br1[i]—Rb1—Br3[iii]	84.255 (10)	Rb2—Br2—Rb2[vi]	176.93 (2)
Br1[ii]—Rb1—Br3[iii]	84.255 (10)	Rb2—Br3—Rb1	178.12 (3)
Br1[i]—Rb1—Br3	84.255 (10)	N1—C1—C2	111.6 (3)
Br1[ii]—Rb1—Br3	84.255 (10)	N1—C1—H1A	109.3
Br3[iii]—Rb1—Br3	159.68 (3)	C2—C1—H1A	109.3
Br1[i]—Rb1—Br1[iii]	157.67 (2)	N1—C1—H1B	109.3
Br1[ii]—Rb1—Br1[iii]	91.481 (16)	C2—C1—H1B	109.3
Br3[iii]—Rb1—Br1[iii]	98.498 (12)	H1A—C1—H1B	108.0
Br3—Rb1—Br1[iii]	98.498 (12)	N2—C2—C1	110.0 (3)
Br1[i]—Rb1—Br1	91.481 (15)	N2—C2—H2A	109.7
Br1[ii]—Rb1—Br1	157.67 (2)	C1—C2—H2A	109.7
Br3[iii]—Rb1—Br1	98.498 (12)	N2—C2—H2B	109.7
Br3—Rb1—Br1	98.498 (12)	C1—C2—H2B	109.7
Br1[iii]—Rb1—Br1	66.19 (3)	H2A—C2—H2B	108.2
Br3—Rb2—Br3[iv]	155.93 (3)	N2—C3—H3A	109.5
Br3—Rb2—Br2[iv]	81.173 (14)	N2—C3—H3B	109.4
Br3[iv]—Rb2—Br2[iv]	81.173 (13)	H3A—C3—H3B	108.6
Br3—Rb2—Br2	81.172 (13)	C1—N1—C1[vii]	111.7 (4)
Br3[iv]—Rb2—Br2	81.173 (14)	C1—N1—H1N	109.3
Br2[iv]—Rb2—Br2	85.22 (3)	C1[vii]—N1—H1N	109.3
Br3—Rb2—Br2[v]	98.376 (11)	C1—N1—H2N	109.3
Br3[iv]—Rb2—Br2[v]	98.376 (11)	C1[vii]—N1—H2N	109.3
Br2[iv]—Rb2—Br2[v]	176.93 (2)	H1N—N1—H2N	107.9
Br2—Rb2—Br2[v]	91.702 (16)	C3—N2—C2	111.3 (3)
Br3—Rb2—Br2[ii]	98.376 (11)	C3—N2—C2[vii]	111.3 (3)
Br3[iv]—Rb2—Br2[ii]	98.376 (11)	C2—N2—C2[vii]	109.4 (4)

Br2^{iv}—Rb2—Br2^{ii}	91.702 (16)	C3—N2—H3N	108.3
Br2—Rb2—Br2^{ii}	176.93 (2)	C2—N2—H3N	108.3
Br2^{v}—Rb2—Br2^{ii}	91.37 (3)	C2^{vii}—N2—H3N	108.3
N1—C1—C2—N2	−56.8 (4)	C1—C2—N2—C3	−176.8 (3)
C2—C1—N1—C1^{vii}	53.6 (5)	C1—C2—N2—C2^{vii}	59.8 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.91	1.91	2.816 (5)	173
N1—H2N···Br3	0.91	2.49	3.243 (4)	140
N2—H3N···Br1	1.00	2.68	3.448 (4)	134
N2—H3N···Br1^{iii}	1.00	2.68	3.448 (4)	134
O1—H1O···Br2^{viii}	0.87	2.34	3.212 (3)	173
C1—H1A···Br1^{iii}	0.99	3.01	3.717 (4)	129
C1—H1B···Br2^{iv}	0.99	2.92	3.652 (4)	131
C2—H2B···Br1^{iii}	0.99	3.06	3.531 (4)	111
C2—H2B···Br3^{viii}	0.99	2.85	3.560 (4)	130
C3—H3A···Br1^{ix}	0.99	3.03	3.927 (4)	152
C3—H3B···Br3^{x}	0.99	2.79	3.653 (5)	146

Symmetry codes: (iii) −x, −y+1, z; (iv) −x+1, −y+1, z; (viii) x, y+1/2, z+1/2; (ix) −x, −y+1/2, z+1/2; (x) x, y, z+1.

Poly[1-methylpiperizine-1,4-diium [tri-μ-bromido-caesium] hemihydrate] (III)

Crystal data

(C$_5$H$_{14}$N$_2$)[CsBr$_3$]·0.5H$_2$O	D_x = 2.435 Mg m$^{−3}$
M_r = 483.83	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, Amm2	Cell parameters from 2407 reflections
a = 13.610 (3) Å	θ = 2.9–27.5°
b = 9.7201 (19) Å	μ = 11.85 mm$^{−1}$
c = 9.977 (2) Å	T = 93 K
V = 1319.9 (5) Å^3	Block, colourless
Z = 4	0.10 × 0.10 × 0.10 mm
$F(000)$ = 892	

Data collection

Rigaku Pilatus 200K CCD diffractometer	1312 independent reflections
	1293 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.022
Absorption correction: multi-scan (CrysalisPro; Rigaku, 2017)	θ_{max} = 25.4°, θ_{min} = 2.9°
T_{min} = 0.463, T_{max} = 1.000	h = −16→15
3718 measured reflections	k = −11→11
	l = −11→12

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0012P)^2]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.029$	$\Delta\rho_{max} = 0.57$ e Å^{-3}
$S = 0.94$	$\Delta\rho_{min} = -0.70$ e Å^{-3}
1312 reflections	Extinction correction: SHELXL-2014/7
68 parameters	(Sheldrick 2015),
1 restraint	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant	Extinction coefficient: 0.00081 (7)
direct methods	Absolute structure: Parsons *et al.* (2013)
Hydrogen site location: mixed	Absolute structure parameter: 0.016 (7)
H-atom parameters constrained	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cs1	0.0000	0.5000	0.10292 (5)	0.01104 (16)
Cs2	0.5000	0.5000	−0.04771 (5)	0.01285 (16)
Br1	0.0000	0.30234 (7)	0.40657 (7)	0.01341 (18)
Br2	0.5000	0.26080 (7)	0.21347 (7)	0.01513 (17)
Br3	0.25365 (6)	0.5000	0.03902 (7)	0.01354 (16)
C1	0.2714 (4)	0.6276 (5)	0.3848 (5)	0.0140 (11)
H1A	0.2128	0.6348	0.3263	0.017*
H1B	0.3132	0.7093	0.3686	0.017*
C2	0.2391 (4)	0.6259 (4)	0.5301 (6)	0.0138 (10)
H2A	0.2977	0.6263	0.5890	0.017*
H2B	0.2001	0.7095	0.5497	0.017*
C3	0.1412 (5)	0.5000	0.6985 (7)	0.0189 (16)
H3A	0.1014	0.4149	0.7140	0.028*
H3B	0.1974	0.5000	0.7625	0.028*
N1	0.3276 (4)	0.5000	0.3497 (6)	0.0125 (13)
H1N	0.3408	0.5000	0.2603	0.015*
H2N	0.3859	0.5000	0.3944	0.015*
N2	0.1782 (4)	0.5000	0.5586 (6)	0.0112 (12)
H3N	0.1205	0.5000	0.4965	0.013*
O1	0.5000	0.5000	0.5110 (6)	0.0149 (16)
H1O	0.5000	0.5749	0.5620	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0133 (4)	0.0096 (3)	0.0102 (3)	0.000	0.000	0.000
Cs2	0.0146 (3)	0.0134 (3)	0.0105 (3)	0.000	0.000	0.000

Br1	0.0155 (4)	0.0110 (3)	0.0138 (3)	0.000	0.000	0.0029 (3)
Br2	0.0193 (4)	0.0128 (3)	0.0133 (3)	0.000	0.000	−0.0001 (3)
Br3	0.0143 (3)	0.0140 (3)	0.0123 (4)	0.000	−0.0017 (3)	0.000
C1	0.015 (3)	0.009 (2)	0.018 (3)	0.001 (2)	0.001 (2)	0.003 (2)
C2	0.017 (3)	0.009 (2)	0.016 (2)	0.002 (2)	0.000 (2)	0.001 (3)
C3	0.021 (4)	0.026 (4)	0.009 (3)	0.000	0.003 (4)	0.000
N1	0.010 (3)	0.016 (3)	0.012 (3)	0.000	0.001 (2)	0.000
N2	0.012 (3)	0.012 (3)	0.010 (3)	0.000	0.001 (2)	0.000
O1	0.022 (4)	0.007 (3)	0.016 (4)	0.000	0.000	0.000

Geometric parameters (Å, º)

Cs1—Br1[i]	3.5319 (9)	C1—C2	1.515 (7)
Cs1—Br1[ii]	3.5319 (9)	C1—H1A	0.9900
Cs1—Br1[iii]	3.5873 (10)	C1—H1B	0.9900
Cs1—Br1	3.5873 (10)	C2—N2	1.505 (6)
Cs1—Br3[iii]	3.5105 (11)	C2—H2A	0.9900
Cs1—Br3	3.5105 (11)	C2—H2B	0.9900
Cs2—Br2[iv]	3.4923 (10)	C3—N2	1.484 (9)
Cs2—Br2	3.4923 (10)	C3—H3A	1.0011
Cs2—Br2[v]	3.4790 (9)	C3—H3B	0.9961
Cs2—Br2[ii]	3.4790 (9)	N1—C1[vii]	1.499 (6)
Cs2—Br3	3.4627 (11)	N1—H1N	0.9100
Cs2—Br3[iv]	3.4627 (11)	N1—H2N	0.9100
Br1—Cs1[vi]	3.5319 (9)	N2—C2[vii]	1.505 (6)
Br2—Cs2[vi]	3.4790 (9)	N2—H3N	1.0000
C1—N1	1.499 (6)	O1—H1O	0.8883
Br3[iii]—Cs1—Br3	159.07 (3)	Cs1[vi]—Br1—Cs1	156.07 (2)
Br3[iii]—Cs1—Br1[i]	84.218 (9)	Cs2[vi]—Br2—Cs2	174.97 (3)
Br3—Cs1—Br1[i]	84.219 (9)	Cs2—Br3—Cs1	175.99 (3)
Br3[iii]—Cs1—Br1[ii]	84.218 (9)	N1—C1—C2	111.3 (4)
Br3—Cs1—Br1[ii]	84.219 (9)	N1—C1—H1A	109.4
Br1[i]—Cs1—Br1[ii]	112.63 (3)	C2—C1—H1A	109.4
Br3[iii]—Cs1—Br1[iii]	98.823 (12)	N1—C1—H1B	109.4
Br3—Cs1—Br1[iii]	98.822 (12)	C2—C1—H1B	109.4
Br1[i]—Cs1—Br1[iii]	156.07 (2)	H1A—C1—H1B	108.0
Br1[ii]—Cs1—Br1[iii]	91.305 (15)	N2—C2—C1	110.4 (4)
Br3[iii]—Cs1—Br1	98.823 (12)	N2—C2—H2A	109.6
Br3—Cs1—Br1	98.822 (13)	C1—C2—H2A	109.6
Br1[i]—Cs1—Br1	91.305 (15)	N2—C2—H2B	109.6
Br1[ii]—Cs1—Br1	156.07 (2)	C1—C2—H2B	109.6
Br1[iii]—Cs1—Br1	64.76 (3)	H2A—C2—H2B	108.1
Br3—Cs2—Br3[iv]	151.06 (3)	N2—C3—H3A	109.2
Br3—Cs2—Br2[v]	99.854 (11)	N2—C3—H3B	110.0
Br3[iv]—Cs2—Br2[v]	99.854 (11)	H3A—C3—H3B	108.5
Br3—Cs2—Br2[ii]	99.854 (11)	C1[vii]—N1—C1	111.7 (5)
Br3[iv]—Cs2—Br2[ii]	99.854 (11)	C1[vii]—N1—H1N	109.3

Br2^v—Cs2—Br2^{ii}	93.55 (3)	C1—N1—H1N	109.3
Br3—Cs2—Br2^{iv}	79.254 (13)	C1^{vii}—N1—H2N	109.3
Br3^{iv}—Cs2—Br2^{iv}	79.255 (13)	C1—N1—H2N	109.3
Br2^v—Cs2—Br2^{iv}	174.97 (3)	H1N—N1—H2N	107.9
Br2^{ii}—Cs2—Br2^{iv}	91.485 (16)	C3—N2—C2	111.4 (4)
Br3—Cs2—Br2	79.254 (13)	C3—N2—C2^{vii}	111.4 (4)
Br3^{iv}—Cs2—Br2	79.255 (13)	C2—N2—C2^{vii}	108.8 (5)
Br2^v—Cs2—Br2	91.485 (16)	C3—N2—H3N	108.4
Br2^{ii}—Cs2—Br2	174.97 (3)	C2—N2—H3N	108.4
Br2^{iv}—Cs2—Br2	83.48 (3)	C2^{vii}—N2—H3N	108.4
N1—C1—C2—N2	−57.1 (6)	C1—C2—N2—C3	−176.9 (4)
C2—C1—N1—C1^{vii}	53.6 (7)	C1—C2—N2—C2^{vii}	60.0 (7)

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2N···O1	0.91	1.94	2.845 (7)	173
N1—H1N···Br3	0.91	2.51	3.259 (6)	140
N2—H3N···Br1	1.00	2.68	3.446 (5)	134
N2—H3N···Br1^{iii}	1.00	2.68	3.446 (5)	134
O1—H1O···Br2^{viii}	0.89	2.36	3.242 (4)	175
C1—H1A···Br1^{iii}	0.99	3.07	3.762 (5)	128
C1—H1B···Br2^{iv}	0.99	2.99	3.712 (5)	131
C2—H2B···Br1^{iii}	0.99	3.08	3.550 (5)	111
C2—H2B···Br3^{viii}	0.99	2.92	3.643 (4)	131
C3—H3B···Br3^{ix}	1.00	2.86	3.726 (7)	145

Symmetry codes: (iii) −x, −y+1, z; (iv) −x+1, −y+1, z; (viii) x, y+1/2, z+1/2; (ix) x, y, z+1.