Syntheses and structures of piperazin-1-ium ABr_2 (A = Cs or Rb): hybrid solids containing 'curtain wall' layers of face- and edge-sharing ABr_6 trigonal prisms

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The isostructural title compounds, poly[piperazin-1-ium [di-μ-bromido-caesium]], $\{(C_4H_{11}N_2)[CsBr_2]\}_n$, and poly[piperazin-1-ium [di-μ-bromido-rubidium]], $\{(C_4H_{11}N_2)[RbBr_2]\}_n$, contain singly-protonated piperazin-1-ium cations and unusual ABr_6 (A = Cs or Rb) trigonal prisms. The prisms are linked into a distinctive 'curtain wall' arrangement propagating in the (010) plane by face and edge sharing. In each case, a network of N—H···N, N—H···Br and N—H···(Br,Br) hydrogen bonds consolidates the structure.

1. Chemical context

Oxide perovskites of generic formula ABO_3, where A and B are metal ions, have been studied for decades because of their physical properties and structural variety (Tilley, 2016). The aristotype (highest-possible symmetry) for this familiar structure type is a cubic network (space group $Pm\bar{3}m$) of vertex-sharing, regular, BO_6 octahedra encapsulating the A cations in 12-coordinate cavities bounded by eight octahedra, but lower symmetry structures are very common (Woodward, 1997). More recently, 'hybrid' RMX_3 perovskites containing organic cations and MX_3 (M = Pb, Sn...; X = halide ion) octahedral networks have attracted intense interest because of their remarkable photophysical properties (Xu et al., 2019; Stylianakis et al., 2019; Zuo et al., 2019). A number of different organic cations occur in these hybrid structures, one of which is the doubly protonated $C_4H_{12}N_2^{2+}$ piperizinium (or piper-azin-1,4-diium) ion as found in the $C_4H_{12}N_2 \cdot ACl_3 \cdot H_2O$ (A = K, Rb, Cs) family (Paton & Harrison, 2010) and $C_4H_{12}N_2 \cdot NaI_3$ (Chen et al., 2018).

(I) A = Cs

(II) A = Rb
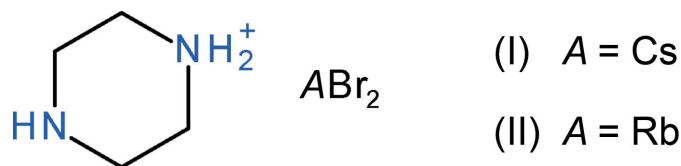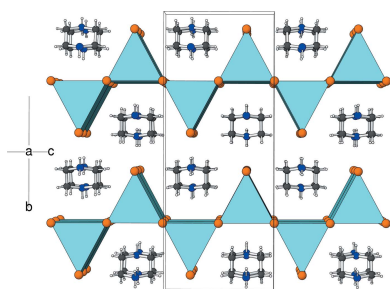
As an extension of these studies, we now describe the title hybrid compounds, containing the singly protonated $C_4H_{11}N_2^+$ piperazin-1-ium cation, which have a generic formula of RMX_2 and totally different crystal structures to RMX_3 hybrid perovskites.

Cs1—Br2^{iii}	3.5157 (5)	Cs1—Br1	3.6228 (6)
Cs1—Br2	3.5801 (5)	Cs1—Br1^{iii}	3.6392 (7)

Symmetry code: (iii) $x - 1, y, z$.

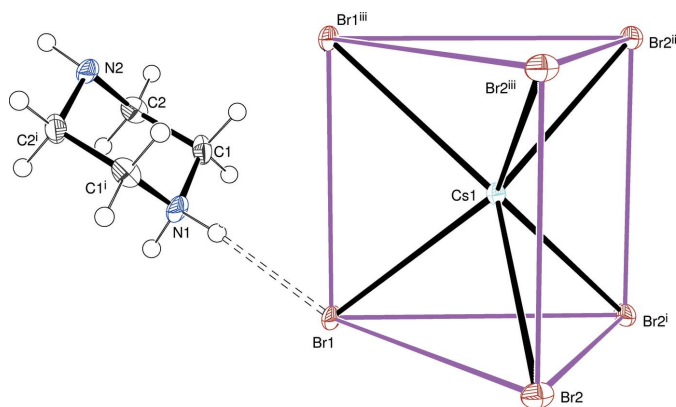| Rb1—Br2^{iii}	3.4157 (8)	Rb1—Br1	3.5013 (9)
Rb1—Br2	3.4659 (8)	Rb1—Br1^{iii}	3.5068 (9)

Symmetry code: (iii) $x - 1, y, z$.

2. Structural commentary

Compounds (I) and (II) are isostructural and crystallize in the orthorhombic space group *Pbcm*. The smaller unit-cell volume (by 5.3%) of (II) presumably reflects the smaller ionic radius (Shannon, 1976) of the Rb$^+$ cation ($r = 1.66$ Å) compared to Cs$^+$ ($r = 1.81$ Å). This structure description will focus on (I) and note significant differences for (II) where applicable.

The asymmetric unit of (I) consists of two methylene groups, an NH group and an NH$_2^+$ group; both nitrogen atoms and their attached H atoms lie on a (001) crystallographic mirror plan (at $z = 1/4$ for the asymmetric atoms). The structure is completed by a caesium atom [site symmetry $m(001)$, Wyckoff site 4d] and two bromine atoms: Br1 [$m(001)$; 4d] and Br2 (2[100]; 4c). The structure of (I) is shown in (Fig. 1).

The complete C$_4$H$_{11}$N$_2^+$ cation is generated by reflection to result in a typical (Brüning *et al.*, 2009) chair conformation for the ring: N1 and N2 deviate from the mean plane of C1/C2/C1^i/C2^i [symmetry code: (i) $x, y, \frac{1}{2} - z$] by 0.656 (5) and −0.682 (4) Å, respectively. The H atom of the neutral N2—H3N group has an equatorial orientation with respect to the ring.

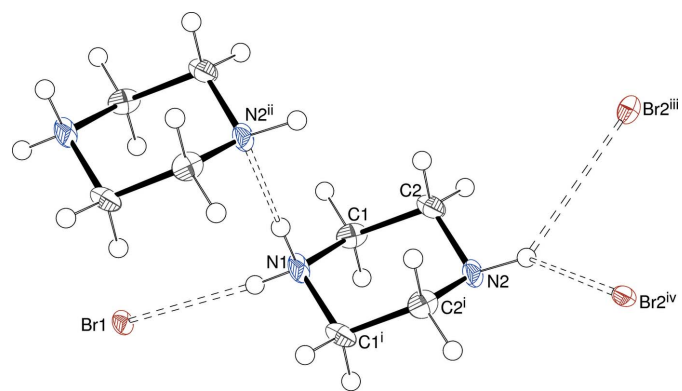The caesium coordination polyhedron in (I) is completed by crystal symmetry, resulting in a distinctive CsBr$_6$ trigonal prism (Fig. 1): the prism has longitudinal (001) mirror symmetry, with the Br1 atoms and the metal atom lying on the mirror. The mean Cs—Br bond length based on four distinct Cs—Br bonds (Table 1) is 3.573 Å [mean Rb—Br bond length for (II) = 3.461 Å; Table 2]. These data may be compared with the shortest Cs—Br separation of 3.716 Å in CsBr (8-coordinate caesium chloride structure) and the shortest Rb—Br separation of 3.427 Å in RbBr (6-coordinate rocksalt structure).

In (I), the prism ends (Br1/Br2/Br2^i and Br1^{iii}/Br2^{ii}/Br2^{iii}; see Fig. 1 for symmetry codes) are parallel by symmetry and separated by 4.5787 (8) Å, *i.e.*, the a unit-cell parameter, hence there is no twisting of the end faces and the Br···Br···Br angles vary from 56.65 (1)–61.68 (1)° [the equivalent prism-end separation for (II) is 4.4675 (13) Å]. The caesium cation in (I) is not quite equidistant from the prism-ends mentioned in the previous sentence, being displaced from them by 2.3177 (6) and 2.2605 (5) Å, respectively. The equivalent data for the Rb atom in (II) are 2.2581 (9) and 2.2091 (9) Å, respectively. The bond-valence sum (BVS) for Cs1 (in valence units) using the formalism of Brese & O'Keeffe (1991) in (I) is 1.12 and the equivalent value for Rb1 in (II) is 0.95 (expected value in both cases = 1.00). This indicates that the bond valences of these cations are satisfied without notable under-bonding or overbonding in these unusual coordination environments.

It may be finally noted that the bromide ions have very different coordination environments: Br1 bridges to two metal atoms [Cs1—Br1—Cs1^{iv} = 78.17 (2) in (I); Rb1—Br1—Rb1^{iv} = 79.21 (3)° in (II); symmetry code: (iv) $x + 1, y, z$] whereas Br2 has an unusual distorted square planar BrCs$_4$ arrangement: the cis Cs—Br2—Cs bond angles in (I) vary between 80.367 (13) and 100.865 (16)°; the five atoms are exactly co-planar by symmetry.

3. Supramolecular features

The extended structure of (I) is consolidated by hydrogen bonds (Fig. 2, Table 3. The N1—H1N···N2 bond from the protonated NH$_2^+$ group to the unprotonated N atom in an

Figure 1
The asymmetric unit of (I) showing 50% displacement ellipsoids expanded to show the complete organic cation and the caesium coordination polyhedron. The N—H···Br hydrogen bond is shown as a double-dashed line. The purple lines linking the bromine atoms emphasize the trigonal–prismatic shape of the CsBr$_6$ polyhedron. Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $x - 1, y, \frac{1}{2} - z$; (iii) $x - 1, y, z$.

Figure 2
Detail of the structure of (I) showing the hydrogen-bonding environment of the C$_4$H$_{11}$N$_2^+$ cation; symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, z + \frac{1}{2}$; (iv) $-x, -y + 1, -z$.

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$N\cdots$N2^{ii}	0.92 (4)	1.95 (4)	2.868 (4)	179 (3)
N1—H2$N\cdots$Br1	0.84 (4)	2.45 (4)	3.284 (3)	174 (4)
N2—H3$N\cdots$Br2^{iii}	0.95 (4)	3.07 (3)	3.756 (2)	130 (1)
N2—H3$N\cdots$Br2^{iv}	0.95 (4)	3.07 (3)	3.756 (2)	130 (1)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$N\cdots$N2^{ii}	0.91	1.92	2.825 (6)	179
N1—H1$N\cdots$Br1	0.91	2.40	3.300 (4)	171
N2—H3$N\cdots$Br2^{iii}	0.94	3.07	3.762 (3)	131
N2—H3$N\cdots$Br2^{iv}	0.94	3.07	3.762 (3)	131

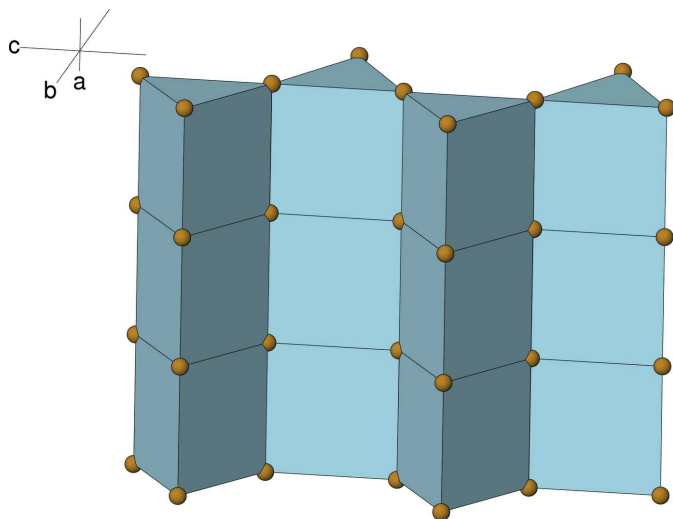Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x, -y + 1, z + \frac{1}{2}$; (iv) $-x, -y + 1, -z$.

adjacent molecule links the organic cations into [100] chains with adjacent cations related by translation symmetry and the N1—H2$N\cdots$Br1 bond connects the organic cation to the inorganic network. The neutral N2—H3N moiety forms a bifurcated N—H$\cdots$(Br2,Br2) hydrogen bond; the H$\cdots$Br contacts are long at 3.07 (3) Å but given their apparent role in bridging the (010) CsBr$_2$ layers we judge them to be structurally significant. The hydrogen-bonding scheme for (II) (Table 4) is almost identical to that in (I).

The CsBr$_6$ prisms in (I) are linked into a striking (010) 'curtain wall' arrangement (Fig. 3) by face sharing in the [100] direction and edge sharing (*via* a pair of Br2 atoms) in the [001] direction; the Cs$\cdots$Cs separation through the prism-ends is 4.5787 (8) Å (by the symmetry operations $x + 1, y, z$ and $x - 1, y, z$) and the separation between metal ions in adjacent columns is 5.42014 (12) Å (symmetry operations $x, \frac{1}{2} - y, -z$ and $x, \frac{1}{2} - y, \frac{1}{2} + z$). The equivalent data for the Rb atoms in (II) are 4.4675 (13) and 5.2338 (14) Å, respectively. When

viewed down [100], the prisms adopt a 'saw-tooth' arrangement with respect to the [010] direction, with alternating columns of prisms pointing 'up' and 'down' (Fig. 4).

4. Database survey

So far as we are aware, the $R A$Br$_2$ topology of the title compounds is a novel one. A search of the Cambridge Structural Database (CSD, version 5.40, last update 19 May 2019; Groom *et al.*, 2016) for the mono-protonated C$_4$H$_{11}$N$_2^+$ cation returned 55 crystal structures but none of them bear a close resemblance to the title compound. As noted in the chemical context section, the doubly protonated C$_4$H$_{12}$N$_2^{2+}$ species occurs in several hybrid RMX_3 perovskites including C$_4$H$_{12}$N$_2 \cdot A$Cl$_3 \cdot$H$_2$O with A = K (CSD refcode GUYMIX), Rb (GUYMOD) and Cs (GUYMUJ) (Paton & Harrison, 2010) and C$_4$H$_{12}$N$_2 \cdot$NaI$_3$ (MEXMAG; Chen *et al.*, 2018).

5. Synthesis and crystallization

Compound (I) was prepared by adding 0.213 g (1.0 mmol) of CsBr and 0.086 g (1.0 mmol) of piperazine to 11.0 ml (1.1 mmol) of a 0.1 *M* HBr solution in a Petri dish to result in a clear solution. Colourless rods of (I) formed after a few days as the water evaporated. Colourless rods of (II) were prepared in the same way, with 0.165 g (1.0 mmol) of RbBr replacing the CsBr. The quantity of acid appears to be critical to the syntheses of (I) and (II): smaller amounts lead to recrystallized CsBr and RbBr and larger amounts lead to different structures containing doubly protonated C$_4$H$_{12}$N$_2^{2+}$ cations.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The N-bonded H atoms were located in difference-Fourier maps: for (I), their positions

Figure 3
Polyhedral view of part of an (010) layer of CsBr$_6$ trigonal prisms in (I).
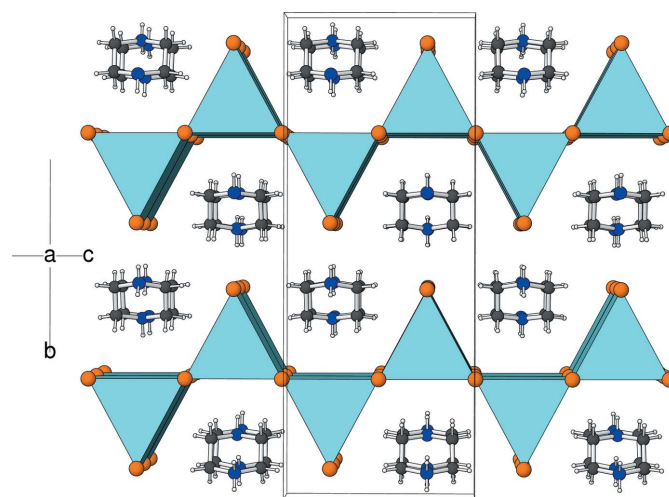
Figure 4
The unit-cell packing in (I) viewed down [100]. Note the 'saw-tooth' arrangement of stacks of CsBr$_6$ prisms with respect to the [001] direction.

research communications

Table 5
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$(C_4H_{11}N_2)[CsBr_2]$	$(C_4H_{11}N_2)[RbBr_2]$
M_r	379.88	332.44
Crystal system, space group	Orthorhombic, $Pbcm$	Orthorhombic, $Pbcm$
Temperature (K)	93	93
a, b, c (Å)	4.5787 (8), 23.325 (5), 9.1828 (17)	4.4675 (13), 23.036 (7), 9.021 (3)
V (Å^3)	980.7 (3)	928.4 (5)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	11.86	13.87
Crystal size (mm)	$0.20 \times 0.05 \times 0.05$	$0.20 \times 0.05 \times 0.05$
Data collection		
Diffractometer	Rigaku Pilatus 200K CCD	Rigaku Pilatus 200K CCD
Absorption correction	Multi-scan (*CrystalClear*; Rigaku, 2013)	Multi-scan (*CrystalClear*; Rigaku, 2013)
T_{min}, T_{max}	0.639, 1.000	0.597, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	11592, 959, 917	11351, 908, 771
R_{int}	0.056	0.086
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.603	0.602
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.055, 1.10	0.023, 0.057, 0.94
No. of reflections	959	908
No. of parameters	55	48
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.34, −0.96	0.74, −0.47

Computer programs: *CrystalClear* (Rigaku, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *ATOMS* (Shape Software, 2005) and *publCIF* (Westrip, 2010).

were freely refined, for (II) they were refined as riding atoms in their as-found relative positions. The C-bound H atoms were placed geometrically (C—H = 0.99 Å) and refined as riding atoms for both structures. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases. The displacement ellipsoids for the C and N atoms in (II) refined to somewhat elongated shapes suggestive of positional disorder of the $C_4H_{11}N_2^+$ cations but attempts to model this did not lead to a significant improvement in fit.

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supporting information

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Computing details

For both structures, data collection: *CrystalClear* (Rigaku, 2013); cell refinement: *CrystalClear* (Rigaku, 2013); data reduction: *CrystalClear* (Rigaku, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Shape Software, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[piperazin-1-ium [di-μ-bromido-caesium]] (I)

Crystal data

$(C_4H_{11}N_2)[CsBr_2]$	$D_x = 2.573$ Mg m^{-3}
$M_r = 379.88$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbcm*	Cell parameters from 3076 reflections
$a = 4.5787$ (8) Å	$\theta = 2.8$–27.5°
$b = 23.325$ (5) Å	$\mu = 11.86$ mm^{-1}
$c = 9.1828$ (17) Å	$T = 93$ K
$V = 980.7$ (3) Å^3	Rod, colourless
$Z = 4$	$0.20 \times 0.05 \times 0.05$ mm
$F(000) = 696$	

Data collection

Rigaku Pilatus 200K CCD diffractometer	959 independent reflections
Radiation source: rotating anode	917 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.056$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2013)	$\theta_{max} = 25.4°$, $\theta_{min} = 3.5°$
	$h = -5 \rightarrow 5$
$T_{min} = 0.639$, $T_{max} = 1.000$	$k = -28 \rightarrow 28$
11592 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.021$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
959 reflections	$\Delta\rho_{max} = 1.34$ e Å^{-3}
55 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
0 restraints	Extinction correction: SHELXL2018 (Sheldrick, 2015),
Primary atom site location: structure-invariant direct methods	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Hydrogen site location: mixed	Extinction coefficient: 0.0010 (2)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cs1	0.02411 (5)	0.31176 (2)	0.250000	0.01125 (13)
Br1	0.52127 (7)	0.43259 (2)	0.250000	0.01635 (15)
Br2	0.53501 (7)	0.250000	0.000000	0.01654 (16)
C1	−0.0049 (5)	0.56445 (11)	0.3834 (4)	0.0205 (7)
H1A	0.120469	0.560779	0.470727	0.025*
H1B	−0.158445	0.534633	0.388670	0.025*
C2	−0.1448 (6)	0.62308 (9)	0.3811 (2)	0.0209 (5)
H2A	−0.267978	0.628079	0.468749	0.025*
H2B	0.008673	0.652975	0.382326	0.025*
N1	0.1740 (7)	0.55578 (12)	0.250000	0.0217 (7)
H1N	0.336 (9)	0.5788 (16)	0.250000	0.026*
H2N	0.251 (8)	0.5231 (17)	0.250000	0.026*
N2	−0.3243 (7)	0.62943 (11)	0.250000	0.0186 (6)
H3N	−0.427 (7)	0.6650 (19)	0.250000	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.01245 (18)	0.00867 (18)	0.01263 (18)	−0.00053 (6)	0.000	0.000
Br1	0.0165 (2)	0.0071 (2)	0.0255 (3)	0.00065 (10)	0.000	0.000
Br2	0.0141 (2)	0.0171 (2)	0.0185 (2)	0.000	0.000	−0.00791 (13)
C1	0.0259 (16)	0.0170 (17)	0.0187 (19)	−0.0048 (8)	−0.0058 (9)	0.0063 (10)
C2	0.0238 (15)	0.0173 (11)	0.0216 (12)	−0.0030 (10)	0.0029 (12)	−0.0062 (9)
N1	0.0218 (19)	0.0067 (14)	0.0367 (16)	0.0036 (12)	0.000	0.000
N2	0.0182 (16)	0.0104 (14)	0.0272 (14)	0.0037 (11)	0.000	0.000

Geometric parameters (Å, º)

Cs1—Br2[i]	3.5157 (5)	C1—H1A	0.9900
Cs1—Br2[ii]	3.5157 (4)	C1—H1B	0.9900
Cs1—Br2[iii]	3.5801 (5)	C2—N2	1.465 (3)
Cs1—Br2	3.5801 (5)	C2—H2A	0.9900
Cs1—Br1	3.6228 (6)	C2—H2B	0.9900
Cs1—Br1[i]	3.6392 (7)	N1—H1N	0.92 (4)
C1—N1	1.488 (4)	N1—H2N	0.84 (4)
C1—C2	1.510 (3)	N2—H3N	0.95 (4)
Br2[i]—Cs1—Br2[ii]	81.534 (14)	N1—C1—C2	110.2 (2)
Br2[i]—Cs1—Br2[iii]	132.072 (12)	N1—C1—H1A	109.6

Br2ⁱⁱ—Cs1—Br2ⁱⁱⁱ	80.366 (13)	C2—C1—H1A	109.6
Br2ⁱ—Cs1—Br2	80.366 (12)	N1—C1—H1B	109.6
Br2ⁱⁱ—Cs1—Br2	132.072 (12)	C2—C1—H1B	109.6
Br2ⁱⁱⁱ—Cs1—Br2	79.768 (14)	H1A—C1—H1B	108.1
Br2ⁱ—Cs1—Br1	135.970 (7)	N2—C2—C1	110.0 (2)
Br2ⁱⁱ—Cs1—Br1	135.970 (7)	N2—C2—H2A	109.7
Br2ⁱⁱⁱ—Cs1—Br1	84.402 (12)	C1—C2—H2A	109.7
Br2—Cs1—Br1	84.401 (13)	N2—C2—H2B	109.7
Br2ⁱ—Cs1—Br1ⁱ	85.085 (12)	C1—C2—H2B	109.7
Br2ⁱⁱ—Cs1—Br1ⁱ	85.085 (13)	H2A—C2—H2B	108.2
Br2ⁱⁱⁱ—Cs1—Br1ⁱ	136.466 (7)	C1—N1—C1ⁱⁱⁱ	110.9 (3)
Br2—Cs1—Br1ⁱ	136.466 (7)	C1—N1—H1N	111.5 (11)
Br1—Cs1—Br1ⁱ	78.173 (18)	C1ⁱⁱⁱ—N1—H1N	111.5 (11)
Cs1—Br1—Cs1ⁱᵛ	78.173 (17)	C1—N1—H2N	110.7 (13)
Cs1ⁱᵛ—Br2—Cs1ᵛ	100.865 (16)	C1ⁱⁱⁱ—N1—H2N	110.7 (13)
Cs1ⁱᵛ—Br2—Cs1ᵛⁱ	178.768 (8)	H1N—N1—H2N	101 (3)
Cs1ᵛ—Br2—Cs1ᵛⁱ	80.367 (13)	C2ⁱⁱⁱ—N2—C2	110.5 (3)
Cs1ⁱᵛ—Br2—Cs1	80.366 (13)	C2ⁱⁱⁱ—N2—H3N	111.4 (10)
Cs1ᵛ—Br2—Cs1	178.768 (8)	C2—N2—H3N	111.4 (10)
Cs1ᵛⁱ—Br2—Cs1	98.402 (15)		
N1—C1—C2—N2	57.7 (3)	C1—C2—N2—C2ⁱⁱⁱ	−60.2 (3)
C2—C1—N1—C1ⁱⁱⁱ	−55.9 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N2ⁱᵛ	0.92 (4)	1.95 (4)	2.868 (4)	179 (3)
N1—H2*N*···Br1	0.84 (4)	2.45 (4)	3.284 (3)	174 (4)
N2—H3*N*···Br2ᵛⁱⁱ	0.95 (4)	3.07 (3)	3.756 (2)	130 (1)
N2—H3*N*···Br2ᵛⁱⁱⁱ	0.95 (4)	3.07 (3)	3.756 (2)	130 (1)

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

Poly[piperazin-1-ium [di-*μ*-bromido-rubidium]] (II)

Crystal data

(C₄H₁₁N₂)[RbBr₂]	D_x = 2.378 Mg m⁻³
M_r = 332.44	Mo *Kα* radiation, *λ* = 0.71073 Å
Orthorhombic, *Pbcm*	Cell parameters from 1939 reflections
a = 4.4675 (13) Å	*θ* = 2.9–27.5°
b = 23.036 (7) Å	*μ* = 13.87 mm⁻¹
c = 9.021 (3) Å	*T* = 93 K
V = 928.4 (5) Å³	Rod, colourless
Z = 4	0.20 × 0.05 × 0.05 mm
F(000) = 624	

Data collection

Rigaku Pilatus 200K CCD diffractometer	908 independent reflections
Radiation source: rotating anode	771 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.086$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2013)	$\theta_{max} = 25.3°$, $\theta_{min} = 2.9°$
$T_{min} = 0.597$, $T_{max} = 1.000$	$h = -5 \rightarrow 5$
11351 measured reflections	$k = -27 \rightarrow 25$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.023$	H-atom parameters constrained
$wR(F^2) = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
$S = 0.94$	where $P = (F_o^2 + 2F_c^2)/3$
908 reflections	$(\Delta/\sigma)_{max} < 0.001$
48 parameters	$\Delta\rho_{max} = 0.74$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.47$ e Å^{-3}

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	0.02991 (9)	0.30763 (2)	0.250000	0.01411 (14)
Br1	0.52893 (9)	0.42482 (2)	0.250000	0.01792 (15)
Br2	0.53856 (10)	0.250000	0.000000	0.02184 (16)
C1	0.0103 (9)	0.56211 (19)	0.3859 (5)	0.0433 (13)
H1A	−0.150237	0.532584	0.391919	0.052*
H1B	0.138441	0.558250	0.474894	0.052*
C2	−0.1233 (9)	0.62095 (17)	0.3812 (4)	0.0371 (10)
H2A	−0.247265	0.627233	0.470786	0.045*
H2B	0.037661	0.650481	0.380468	0.045*
N1	0.1926 (10)	0.55235 (19)	0.250000	0.0490 (17)
H1N	0.264148	0.515363	0.250000	0.059*
H2N	0.351831	0.577000	0.250001	0.059*
N2	−0.3067 (9)	0.62729 (18)	0.250000	0.0358 (12)
H3N	−0.409568	0.662828	0.250000	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0154 (2)	0.0163 (3)	0.0106 (2)	−0.00032 (16)	0.000	0.000
Br1	0.0178 (3)	0.0145 (3)	0.0215 (3)	0.00069 (17)	0.000	0.000
Br2	0.0161 (3)	0.0330 (3)	0.0165 (3)	0.000	0.000	−0.01151 (19)

C1	0.050 (3)	0.045 (3)	0.035 (2)	−0.027 (2)	−0.031 (2)	0.024 (2)
C2	0.047 (2)	0.038 (2)	0.027 (2)	−0.024 (2)	0.020 (2)	−0.0183 (18)
N1	0.018 (2)	0.010 (2)	0.118 (6)	0.0018 (18)	0.000	0.000
N2	0.020 (2)	0.018 (2)	0.070 (4)	0.0028 (18)	0.000	0.000

Geometric parameters (Å, º)

Rb1—Br2^i	3.4157 (8)	C1—H1A	0.9900
Rb1—Br2^{ii}	3.4157 (8)	C1—H1B	0.9900
Rb1—Br2	3.4659 (8)	C2—N2	1.447 (5)
Rb1—Br2^{iii}	3.4659 (8)	C2—H2A	0.9900
Rb1—Br1	3.5013 (9)	C2—H2B	0.9900
Rb1—Br1^i	3.5068 (9)	N1—H1N	0.9100
C1—C2	1.482 (6)	N1—H2N	0.9100
C1—N1	1.489 (5)	N2—H3N	0.9389
Br2^i—Rb1—Br2^{ii}	82.64 (3)	C2—C1—N1	109.6 (3)
Br2^i—Rb1—Br2	80.96 (2)	C2—C1—H1A	109.8
Br2^{ii}—Rb1—Br2	134.60 (2)	N1—C1—H1A	109.8
Br2^i—Rb1—Br2^{iii}	134.60 (2)	C2—C1—H1B	109.8
Br2^{ii}—Rb1—Br2^{iii}	80.96 (2)	N1—C1—H1B	109.8
Br2—Rb1—Br2^{iii}	81.19 (3)	H1A—C1—H1B	108.2
Br2^i—Rb1—Br1	135.144 (12)	N2—C2—C1	110.1 (3)
Br2^{ii}—Rb1—Br1	135.143 (12)	N2—C2—H2A	109.6
Br2—Rb1—Br1	82.98 (2)	C1—C2—H2A	109.6
Br2^{iii}—Rb1—Br1	82.984 (19)	N2—C2—H2B	109.6
Br2^i—Rb1—Br1^i	83.63 (2)	C1—C2—H2B	109.6
Br2^{ii}—Rb1—Br1^i	83.63 (2)	H2A—C2—H2B	108.2
Br2—Rb1—Br1^i	135.505 (12)	C1—N1—C1^{iii}	110.8 (4)
Br2^{iii}—Rb1—Br1^i	135.505 (13)	C1—N1—H1N	109.5
Br1—Rb1—Br1^i	79.21 (3)	C1^{iii}—N1—H1N	109.5
Rb1—Br1—Rb1^{iv}	79.21 (3)	C1—N1—H2N	109.5
Rb1^{iv}—Br2—Rb1^v	100.02 (3)	C1^{iii}—N1—H2N	109.5
Rb1^{iv}—Br2—Rb1^{vi}	179.021 (14)	H1N—N1—H2N	108.1
Rb1^v—Br2—Rb1^{vi}	80.96 (2)	C2—N2—C2^{iii}	109.8 (4)
Rb1^{iv}—Br2—Rb1	80.96 (2)	C2—N2—H3N	111.4
Rb1^v—Br2—Rb1	179.021 (14)	C2^{iii}—N2—H3N	111.4
Rb1^{vi}—Br2—Rb1	98.06 (3)		
N1—C1—C2—N2	58.4 (4)	C1—C2—N2—C2^{iii}	−62.1 (5)
C2—C1—N1—C1^{iii}	−55.3 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H2*N*⋯N2^{iv}	0.91	1.92	2.825 (6)	179
N1—H1*N*⋯Br1	0.91	2.40	3.300 (4)	171

N2—H3*N*···Br2[vii]	0.94	3.07	3.762 (3)	131
N2—H3*N*···Br2[viii]	0.94	3.07	3.762 (3)	131

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