# 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

Kirstie A. Rickaby,[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, St Andrews KY16 9ST, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

The isostructural title compounds, poly[piperazin-1-ium [di-$\mu$-bromido-caesium]], $\{(C_4H_{11}N_2)[CsBr_2]\}_n$, and poly[piperazin-1-ium [di-$\mu$-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 piperazin-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
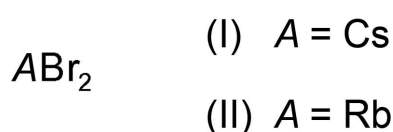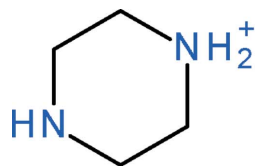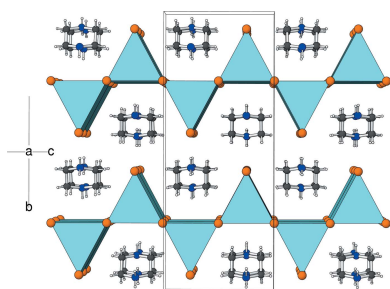
As an extension of these studies, we now describe the title hybrid compounds, containing the singly protonated $C_4H_{11}N_2^+$ piperazin-1-ium cation, which have a generic formula of $RMX_2$ and totally different crystal structures to $RMX_3$ hybrid perovskites.

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

| 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) $x - 1, y, z$.

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

| 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 4$d$] and two bromine atoms: Br1 [$m(001)$; 4$d$] and Br2 (2[100]; 4$c$). 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—H3$N$ 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 underbonding 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 coplanar by symmetry.

## 3. Supramolecular features

The extended structure of (I) is consolidated by hydrogen bonds (Fig. 2, Table 3. The N1—H1$N$···N2 bond from the protonated NH$_2^+$ group to the unprotonated N atom in an
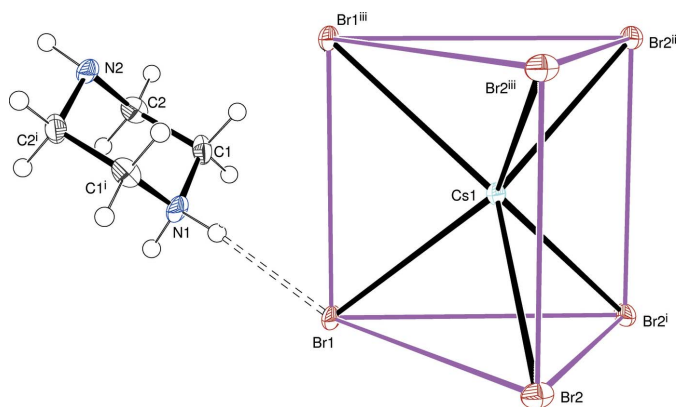


**Figure 1**
The asymmetric unit of (I) showing 50% displacement ellipsoids expanded to show the complete organic cation and the caesium coordination polyhedron. The N—H···Br hydrogen bond is shown as a double-dashed line. The purple lines linking the bromine atoms emphasize the trigonal–prismatic shape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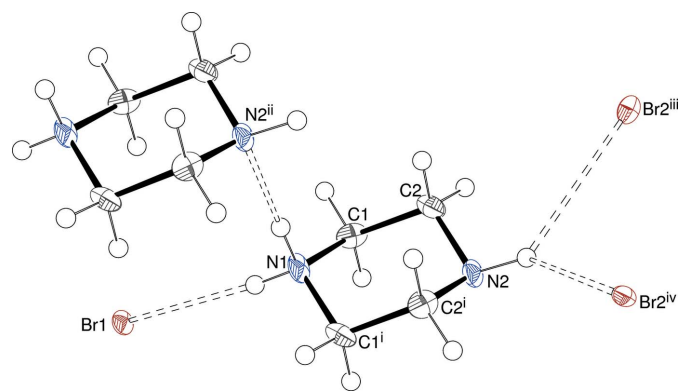


**Figure 2**
Detail of the structure of (I) showing the hydrogen-bonding environment of the C$_4$H$_{11}$N$_2^+$ cation; symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, z + \frac{1}{2}$; (iv) $-x, -y + 1, -z$.

**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 |

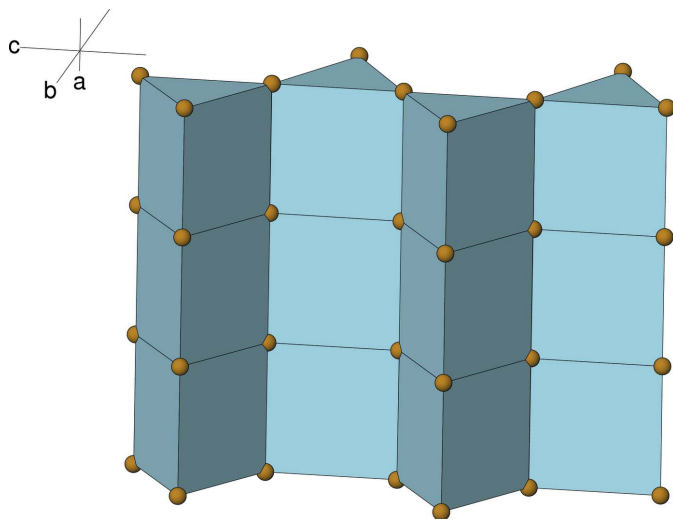Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x, -y + 1, z + \frac{1}{2}$; (iv) $-x, -y + 1, -z$.

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—H3$N$ 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 $RA$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$_2$·$A$Cl$_3$·H$_2$O with $A$ = K (CSD refcode GUYMIX), Rb (GUYMOD) and Cs (GUYMUJ) (Paton & Harrison, 2010) and C$_4$H$_{12}$N$_2$·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



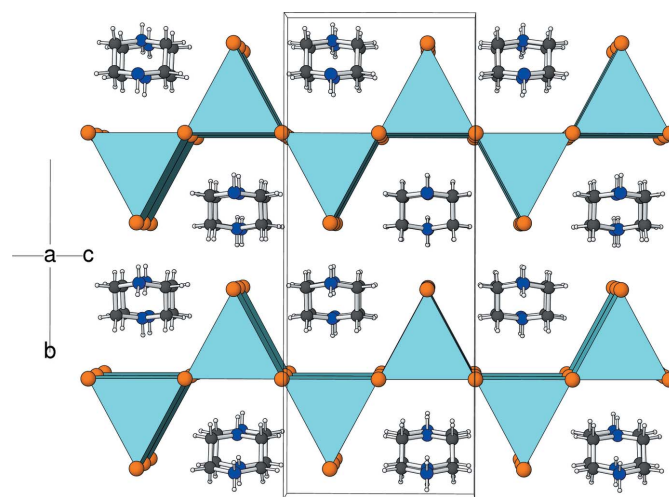**Figure 3**
Polyhedral view of part of an (010) layer of CsBr$_6$ trigonal prisms in (I).



**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.

**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 $K\alpha$ |
| $\mu$ (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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Zuo, T. T., He, X. X., Hu, P. & Jiang, H. (2019). *ChemNanoMat*, **5**, 278–289.

# supporting information

## Syntheses and structures of piperazin-1-ium *A*Br$_2$ (*A* = Cs or Rb): hybrid solids containing `curtain wall′ layers of face- and edge-sharing *A*Br$_6$ trigonal prisms

**Kirstie A. Rickaby, Alexandra M. Z. Slawin and William T. A. Harrison**

**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$_4$H$_{11}$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 × 0.05 × 0.05 mm |
| $F(000)$ = 696 | |

*Data collection*

| | |
|---|---|
| Rigaku Pilatus 200K CCD diffractometer | 959 independent reflections |
| Radiation source: rotating anode | 917 reflections with $I > 2\sigma(I)$ |
| $\omega$ 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(2$\theta$)]$^{-1/4}$ |
| 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—H1N⋯N2iv | 0.92 (4) | 1.95 (4) | 2.868 (4) | 179 (3) |
| N1—H2N⋯Br1 | 0.84 (4) | 2.45 (4) | 3.284 (3) | 174 (4) |
| N2—H3N⋯Br2vii | 0.95 (4) | 3.07 (3) | 3.756 (2) | 130 (1) |
| N2—H3N⋯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*

| | |
|---|---|
| $(C_4H_{11}N_2)[RbBr_2]$ | $D_x = 2.378$ Mg m$^{-3}$ |
| $M_r = 332.44$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Orthorhombic, *Pbcm* | Cell parameters from 1939 reflections |
| $a = 4.4675$ (13) Å | $\theta = 2.9$–27.5° |
| $b = 23.036$ (7) Å | $\mu = 13.87$ mm$^{-1}$ |
| $c = 9.021$ (3) Å | $T = 93$ K |
| $V = 928.4$ (5) Å$^3$ | Rod, colourless |
| $Z = 4$ | $0.20 \times 0.05 \times 0.05$ mm |
| $F(000) = 624$ | |

*Data collection*

| | |
|---|---|
| Rigaku Pilatus 200K CCD diffractometer | 908 independent reflections |
| Radiation source: rotating anode | 771 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.086$ |
| Absorption correction: multi-scan (CrystalClear; Rigaku, 2013) | $\theta_{max} = 25.3°$, $\theta_{min} = 2.9°$ |
| | $h = -5\rightarrow5$ |
| $T_{min} = 0.597$, $T_{max} = 1.000$ | $k = -27\rightarrow25$ |
| 11351 measured reflections | $l = -10\rightarrow10$ |

*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) $-x$, $-y+1$, $-z$.