

Piperazin-1-ium triaquadibromidosodium

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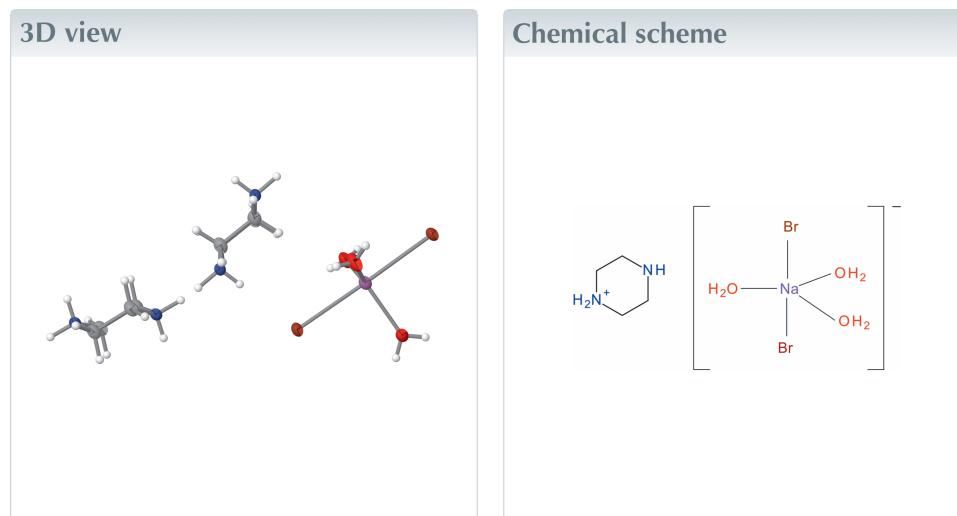
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Keywords: crystal structure; complex ion; sodium; trigonal bipyramid.**CCDC reference:** 2500621**Structural data:** full structural data are available from iucrdata.iucr.org

In the title compound, $(C_4H_{11}N_2)[NaBr_2(H_2O)_3]$, the complete organic cation, which adopts a typical chair conformation, is generated by crystallographic inversion symmetry and one of the N-bonded H atoms is half occupied. The sodium ion (site symmetry m) at the centre of the complex anion adopts a distorted trigonal-bipyramidal coordination geometry with the water molecules in the equatorial sites and the bromide ions in the axial sites. In the extended structure, $O-H \cdots Br$ hydrogen bonds generate a porous ‘honeycomb’ three-dimensional network of complex anions encapsulating [010] channels occupied by the cations, which are linked to each other by $N-H \cdots N$ hydrogen bonds and anchored to the honeycomb network *via* $N-H \cdots Br$ hydrogen bonds.



Structure description

Some time ago we reported a family of ‘hybrid’ organic/inorganic perovskites of general formulae RAX_3 and $RAX_3 \cdot H_2O$ where R is a doubly protonated organic dication such as piperazinium (piperazin-1,4-dium) ($C_4H_{12}N_2^{2+}$) or ‘dabconium’ (1,4-diazoniabicyclo-[2.2.2]octane) ($C_6H_{14}N_2^{2+}$), A is an alkali metal (K^+ , Rb^+ , Cs^+) and X is a halide ion (Cl^- , Br^-) (Paton & Harrison, 2010). These phases consist of a three-dimensional network of corner-sharing AX_6 octahedra analogous to the metal–oxide octahedral framework in inorganic perovskites (Tilley, 2016) with the lacunae occupied by the organic cations, and in some cases, also by water molecules. Other workers (Zhang *et al.*, 2017; Pan *et al.*, 2017; Chen *et al.*, 2018) have substantially expanded this family and shown that some of these phases exhibit striking ferroelectric behaviour akin to that shown by classical oxide perovskites. We later prepared the ‘missing link’ hemihydrate $RABr_3 \cdot 0.5H_2O$ hybrid perovskites (Ferrandin *et al.*, 2019) where R is the 1-methylpiperazine-1,4-dium cation ($C_5H_{14}N_2^{2+}$) and $A = K^+$, Rb^+ or Cs^+ : the known RAX_3 and $RAX_3 \cdot H_2O$ hybrid perovskites were surveyed in this paper. In an attempt to prepare a new hybrid perovskite of putative formula $C_4H_{12}N_2 \cdot NaBr_3 \cdot xH_2O$ we reacted piperazine and acidified sodium bromide in water but instead, the unexpected title compound, $(C_4H_{11}N_2)^+[NaBr_2(H_2O)_3]^-$ (**I**), arose and we now describe its structure.

Table 1
Selected geometric parameters (Å, °).

Na1—O1	2.266 (5)	Na1—O2	2.276 (4)
Na1—O3	2.274 (4)	Na1—Br1	2.9160 (4)
O1—Na1—O3	131.29 (19)	O3—Na1—Br1	89.37 (4)
O1—Na1—O2	113.36 (18)	O2—Na1—Br1	90.73 (4)
O3—Na1—O2	115.36 (19)	Br1—Na1—Br1 ⁱ	178.38 (8)
O1—Na1—Br1	90.03 (4)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

The asymmetric unit of (**I**) (Fig. 1), which crystallizes in the orthorhombic space group *Pnma*, consists of two methylene groups, one NH_{1.5} grouping (the H-atom disorder is described below), one Na⁺ ion (site symmetry *m*), three water molecules (O site symmetries *m*) and one bromide ion. Crystal symmetry (an inversion centre at 0, 1/2, 1 for the asymmetric atoms) generates the complete C₄H₁₁N₂⁺ piperazin-1-ium cation, which adopts a normal chair conformation (Dennington & Weller, 2018) with the N atoms displaced by ±0.631 (6) Å from the plane of the four C atoms. Atom H1A, which has an equatorial orientation with respect to the chair, must be 1/2 occupied, otherwise a chemically unreasonable H1A⋯H1Aⁱ [symmetry code: (i) $x, \frac{3}{2} - y, z$] short contact of ~0.76 Å would arise. This overall mono-protonation of the organic species leads to a disordered N1—H1A⋯N1/N1⋯H1A—N1 hydrogen bond in the extended structure of (**I**) (see below) and (of course) establishes proper charge balance with the complex anion.

The complete [NaBr₂(H₂O)₃][−] complex anion in (**I**) is generated by a mirror plane at $y = 1/4$ for the asymmetric atoms. This results in an unusual distorted trigonal pyramidal coordination geometry for the sodium ion with the O atoms (mean Na—O = 2.272 Å) occupying the equatorial sites and the bromide ions the axial sites. The Br1—Na1—Br1ⁱⁱ [symmetry code: (ii) $x, \frac{1}{2} - y, z$] moiety is almost linear at

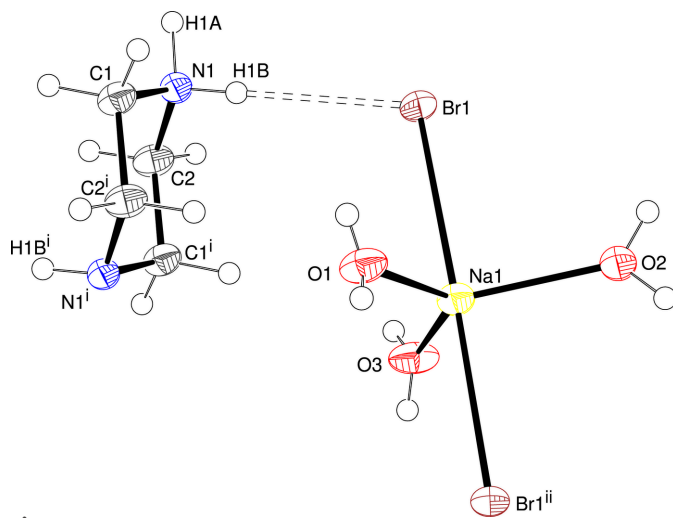


Figure 1
The asymmetric unit of (**I**) expanded to show the complete cation and complex anion showing 50% displacement ellipsoids. The hydrogen bond is shown as a double-dashed line. Symmetry codes: (i) $-x, 1 - y, 2 - z$; (ii) $x, \frac{1}{2} - y, z$. Atom H1A is statistically disordered and is shown in just one location.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H⋯ <i>A</i>	<i>D</i> —H	H⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> —H⋯ <i>A</i>
O1—H1⋯Br1 ⁱⁱ	0.75 (4)	2.65 (4)	3.386 (3)	167 (5)
O2—H2⋯Br1 ⁱⁱⁱ	0.84 (4)	2.52 (4)	3.352 (3)	172 (4)
O3—H3⋯Br1 ^{iv}	0.78 (4)	2.59 (5)	3.365 (3)	170 (5)
N1—H1A⋯N1 ^v	1.01 (7)	1.77 (7)	2.773 (6)	172 (6)
N1—H1B⋯Br1	0.88 (4)	2.59 (4)	3.467 (3)	177 (4)

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

178.38 (8)° while the O—Na—O bond angles (Table 1) show some deviations from ideal local *D*_{3h} symmetry with the minimum and maximum angles being 113.36 (18) and 131.29 (19)°, respectively: the τ₅ parameter (Addison *et al.*, 1984) is 0.78 compared to 1.00 for a regular trigonal-prismatic geometry. The sodium bond-valence sum (BVS) of 1.25 valence units (expected value 1.00 v.u.) using the BVS data collated by Brown (2020), suggests a degree of ‘overbonding’ for the metal ion in (**I**).

In the extended structure of (**I**), the complex anions are linked by O—H⋯Br hydrogen bonds (Table 2). All six water H atoms (three being symmetry generated by the mirror plane) participate in these links. Each water molecule forms a hydrogen bond to an adjacent complex anion both ‘above’ (with respect to the *b*-axis direction) and below it and each bromide ion accepts three such bonds (Fig. 2). Given their H⋯Br lengths and near-linear bond angles, they may be

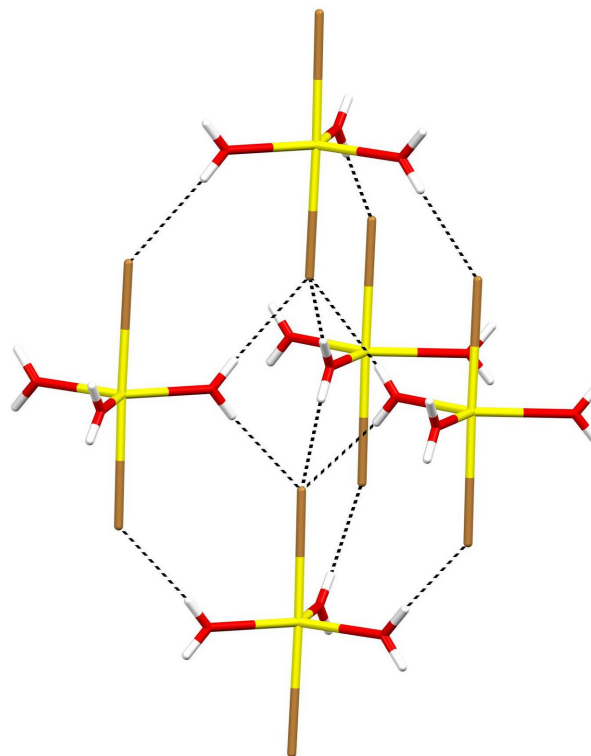


Figure 2
Fragment of the extended structure of (**I**) showing a network of O—H⋯Br hydrogen bonds (black dashed lines) in which each bromide ion accepts three such bonds. The Br[−] ion also accepts an N—H⋯Br hydrogen bond from the organic cation (not shown).

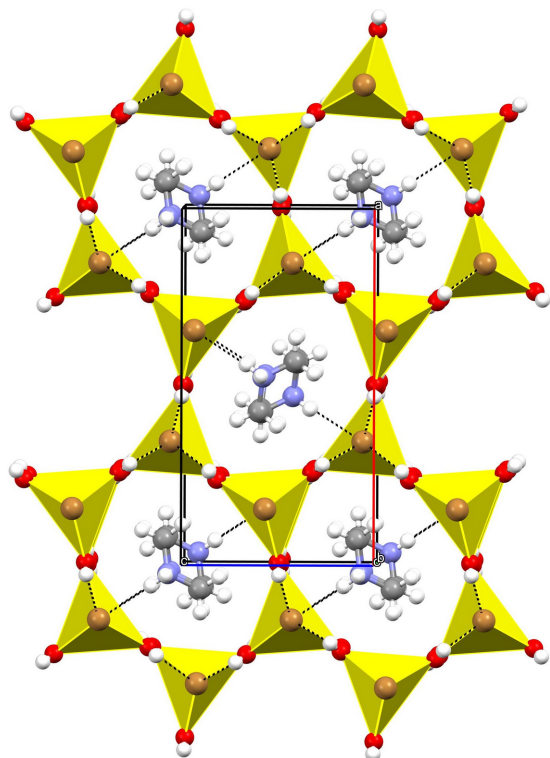


Figure 3

The unit-cell packing in **(I)** viewed down [010] with the cations shown in ball-and-stick representation and the complex anions in polyhedral representation. Hydrogen bonds are shown as black dashed lines.

regarded as strong hydrogen bonds. Collectively, these hydrogen bonds result in a three-dimensional ‘honeycomb’ network encapsulating [010] channels occupied by the organic cations (Fig. 3). As noted above, the cations are linked by disordered N1–H1A···N1 hydrogen bonds into [010] chains and finally, N1–H1B···Br1 hydrogen bonds help to anchor the cations in the [010] channels with respect to the honeycomb framework.

A survey of the Cambridge Structural Database (Groom *et al.*, 2016; updated to October 2025) did not yield any matches for the complex anion reported here. As to why the intended compound did not form, we may speculate that the sodium cation (ionic radius for Na⁺ = 1.02 Å compared to 1.38 Å for K⁺) is too small to permit the formation of a perovskite-like network of corner-sharing NaBr₆ octahedra in a hybrid perovskite. However, it should be noted that sodium bromide is a very well-known phase that contains NaBr₆ octahedra in which the Na–Br separation is about 2.987 Å (Nickels *et al.*, 1949) and it may be the case that we simply failed to find the right synthetic conditions to make the target hybrid perovskite.

Synthesis and crystallization

Compound **(I)** was prepared by mixing 0.43 g of C₄H₁₀N₂, 0.51 g of NaBr, 10 ml of 1.0 M HBr solution and 20 ml of water (piperazine:Na:Br molar ratio ≈ 1:1:3), which resulted in a colourless solution. The solution was left in a Petri dish at

Table 3

Experimental details.

Crystal data	
Chemical formula	(C ₄ H ₁₁ N ₂)[NaBr ₂ (H ₂ O) ₃]
<i>M_r</i>	324.01
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.2622 (12), 10.6066 (8), 7.6876 (6)
<i>V</i> (Å ³)	1162.93 (16)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	6.99
Crystal size (mm)	0.48 × 0.26 × 0.07
Data collection	
Diffractometer	Rigaku R-Axis CCD
Absorption correction	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.400, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	14657, 1400, 1324
<i>R_{int}</i>	0.100
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.045, 0.094, 1.27
No. of reflections	1400
No. of parameters	76
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.67, −1.14

Computer programs: *CrystalClear* (Rigaku, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

room temperature and blade-like colourless crystals of **(I)** formed as the water evaporated over a few days. Mixtures with less added acid led to recrystallized KBr and with more acid produced the known phase (C₄H₁₂N₂)Br₂·H₂O (Bujak, 2015).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The O- and N-bound H atoms were located in difference maps and their positions were freely refined. The C-bound H atoms were located geometrically (C–H = 0.98 Å) and refined as riding atoms. The constraint *U*_{iso}(H) = 1.2*U*_{eq}(carrier) was applied in all cases. Atom H1A is disordered by symmetry about a crystallographic mirror plane: lower-symmetry space groups were investigated to see if an ordered model could be developed but these did not resolve the disorder and the refinements showed excessive correlation between parameters and unrealistic displacement ellipsoids, which are signs that the symmetry is too low, so space group *Pnma* was assumed.

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full crystallographic data

IUCrData (2025). **10**, x250985 [https://doi.org/10.1107/S241431462500985X]

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Crystal data

(C₄H₁₁N₂)[NaBr₂(H₂O)₃]

M_r = 324.01

Orthorhombic, *Pnma*

a = 14.2622 (12) Å

b = 10.6066 (8) Å

c = 7.6876 (6) Å

V = 1162.93 (16) Å³

Z = 4

F(000) = 640

D_x = 1.851 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 6537 reflections

θ = 2.4–27.5°

μ = 6.99 mm⁻¹

T = 120 K

Blade, colourless

0.48 × 0.26 × 0.07 mm

Data collection

Rigaku R-AXIS CCD
diffractometer

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2014)

T_{min} = 0.400, *T_{max}* = 1.000

14657 measured reflections

1400 independent reflections

1324 reflections with *I* > 2σ(*I*)

R_{int} = 0.100

θ_{max} = 27.5°, θ_{min} = 2.9°

h = -18→17

k = -13→13

l = -9→10

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.045

wR(*F*²) = 0.094

S = 1.27

1400 reflections

76 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0241*P*)² + 2.2228*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.67 e Å⁻³

Δρ_{min} = -1.14 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>	Occ. (<1)
Na1	0.16043 (13)	0.250000	0.5630 (3)	0.0249 (5)	

Br1	0.15785 (2)	0.52490 (3)	0.56542 (5)	0.02552 (16)	
O1	0.2377 (3)	0.250000	0.8205 (6)	0.0324 (9)	
H1	0.261 (3)	0.193 (4)	0.860 (6)	0.039*	
O2	0.2576 (3)	0.250000	0.3282 (5)	0.0318 (9)	
H2	0.280 (3)	0.190 (4)	0.272 (6)	0.038*	
O3	0.0046 (3)	0.250000	0.5006 (7)	0.0349 (9)	
H3	-0.030 (3)	0.193 (4)	0.496 (6)	0.042*	
N1	0.0284 (2)	0.6193 (3)	0.9243 (4)	0.0225 (6)	
H1A	0.032 (5)	0.714 (7)	0.914 (9)	0.027*	0.5
H1B	0.063 (3)	0.594 (4)	0.836 (6)	0.027*	
C1	0.0716 (3)	0.5725 (3)	1.0874 (5)	0.0264 (8)	
H1C	0.038009	0.608773	1.188345	0.032*	
H1D	0.137721	0.600804	1.093083	0.032*	
C2	-0.0681 (3)	0.5709 (3)	0.9025 (5)	0.0273 (8)	
H2A	-0.092890	0.598665	0.788475	0.033*	
H2B	-0.108701	0.606976	0.994359	0.033*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0270 (11)	0.0202 (10)	0.0274 (12)	0.000	-0.0015 (8)	0.000
Br1	0.0305 (3)	0.0167 (2)	0.0294 (3)	0.00086 (12)	0.00097 (13)	-0.00139 (12)
O1	0.040 (2)	0.0202 (17)	0.037 (2)	0.000	-0.0077 (19)	0.000
O2	0.041 (2)	0.0203 (17)	0.034 (2)	0.000	0.0109 (18)	0.000
O3	0.027 (2)	0.0203 (17)	0.057 (3)	0.000	-0.0062 (19)	0.000
N1	0.0259 (15)	0.0177 (13)	0.0241 (16)	0.0009 (11)	0.0034 (12)	-0.0004 (11)
C1	0.0308 (19)	0.0205 (17)	0.028 (2)	0.0008 (14)	-0.0043 (15)	-0.0015 (14)
C2	0.0278 (18)	0.0205 (17)	0.034 (2)	0.0018 (14)	-0.0059 (15)	-0.0001 (14)

Geometric parameters (Å, °)

Na1—O1	2.266 (5)	O3—H3 ⁱ	0.78 (4)
Na1—O3	2.274 (4)	N1—C2	1.479 (5)
Na1—O2	2.276 (4)	N1—C1	1.482 (4)
Na1—Br1	2.9160 (4)	N1—H1A	1.01 (7)
Na1—Br1 ⁱ	2.9161 (4)	N1—H1B	0.88 (4)
O1—H1	0.75 (4)	C1—C2 ⁱⁱ	1.524 (5)
O1—H1 ⁱ	0.75 (4)	C1—H1C	0.9900
O2—H2	0.84 (4)	C1—H1D	0.9900
O2—H2 ⁱ	0.84 (4)	C2—H2A	0.9900
O3—H3	0.78 (4)	C2—H2B	0.9900
O1—Na1—O3	131.29 (19)	C2—N1—C1	111.5 (3)
O1—Na1—O2	113.36 (18)	C2—N1—H1A	112 (4)
O3—Na1—O2	115.36 (19)	C1—N1—H1A	112 (4)
O1—Na1—Br1	90.03 (4)	C2—N1—H1B	109 (3)
O3—Na1—Br1	89.37 (4)	C1—N1—H1B	108 (3)
O2—Na1—Br1	90.73 (4)	H1A—N1—H1B	102 (5)

O1—Na1—Br1 ⁱ	90.03 (4)	N1—C1—C2 ⁱⁱ	111.3 (3)
O3—Na1—Br1 ⁱ	89.37 (4)	N1—C1—H1C	109.4
O2—Na1—Br1 ⁱ	90.73 (4)	C2 ⁱⁱ —C1—H1C	109.4
Br1—Na1—Br1 ⁱ	178.38 (8)	N1—C1—H1D	109.4
Na1—O1—H1	124 (4)	C2 ⁱⁱ —C1—H1D	109.4
Na1—O1—H1 ⁱ	124 (4)	H1C—C1—H1D	108.0
H1—O1—H1 ⁱ	107 (7)	N1—C2—C1 ⁱⁱ	111.8 (3)
Na1—O2—H2	130 (3)	N1—C2—H2A	109.3
Na1—O2—H2 ⁱ	130 (3)	C1 ⁱⁱ —C2—H2A	109.3
H2—O2—H2 ⁱ	100 (6)	N1—C2—H2B	109.3
Na1—O3—H3	129 (3)	C1 ⁱⁱ —C2—H2B	109.3
Na1—O3—H3 ⁱ	129 (3)	H2A—C2—H2B	107.9
H3—O3—H3 ⁱ	101 (7)		
C2—N1—C1—C2 ⁱⁱ	54.4 (4)	C1—N1—C2—C1 ⁱⁱ	-54.7 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots Br1 ⁱⁱⁱ	0.75 (4)	2.65 (4)	3.386 (3)	167 (5)
O2—H2 \cdots Br1 ^{iv}	0.84 (4)	2.52 (4)	3.352 (3)	172 (4)
O3—H3 \cdots Br1 ^v	0.78 (4)	2.59 (5)	3.365 (3)	170 (5)
N1—H1A \cdots N1 ^{vi}	1.01 (7)	1.77 (7)	2.773 (6)	172 (6)
N1—H1B \cdots Br1	0.88 (4)	2.59 (4)	3.467 (3)	177 (4)

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