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catena-Poly[hemi(hexane-1,6-diammonium) [[aquadibromidomanganese(II)]-μ-pyridine-2-carboxylato]]

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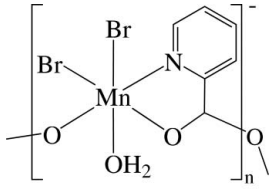
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.031; wR factor = 0.114; data-to-parameter ratio = 17.8.

The asymmetric unit of the title compound, $\{(C_6H_{18}N_2)_{0.5}[MnBr_2(C_6H_4NO_2)(H_2O)]\}_n$, contains the repeat unit of the complex anion and one-half of a hexane-1,6-diammonium cation that is located on a twofold rotation axis. In the anionic polymer, the Mn^{2+} ions are bridged by the pyridinecarboxylate (pic) anion ligand, forming a chain structure along the c axis. The Mn^{2+} ion is six-coordinated in a distorted octahedral environment by one N atom of the pyridine ring, two O atoms of the two carboxylate groups, one O atom of the water molecule and two Br atoms. The compound displays intermolecular N—H···O, N—H···Br, O—H···Br and O—H···O hydrogen bonding. There may also be intermolecular π–π interactions between adjacent pyridine rings, with a centroid–centroid distance of 3.992 (4) Å.

Related literature

For the synthesis and structure of the Mn(III)–pic complex, $[Mn(pic)_3]$, see: Figgis *et al.* (1978); Yamaguchi & Sawyer (1985); Li *et al.* (2000). For the synthesis and structure of the Mn(II)–pic complex, $[Mn(pic)_2(H_2O)_2]$, see: Okabe & Koizumi (1998); Barandika *et al.* (1999). For details of mono-, di- and polynuclear Mn(II, III, IV)–pic complexes, see: Huang *et al.* (2004).



n/2 $[NH_3(CH_2)_6NH_3]^{2+}$

Experimental

Crystal data

$(C_6H_{18}N_2)_{0.5}[MnBr_2(C_6H_4NO_2)(H_2O)]$
M_r = 413.99
Monoclinic, $C2/c$
a = 13.490 (3) Å
b = 21.510 (5) Å
c = 9.803 (2) Å
β = 91.125 (4)°
V = 2843.9 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 6.55 mm^{-1}
T = 293 K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.394, T_{max} = 0.520
7815 measured reflections
2705 independent reflections
1846 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.114
S = 0.94
2705 reflections
152 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1^{i}	0.89	2.44	2.949 (6)	117
N2—H2A···O2^{i}	0.89	2.47	3.300 (6)	155
N2—H2B···Br2^{i}	0.89	2.61	3.339 (4)	139
N2—H2C···Br2^{ii}	0.89	2.58	3.417 (5)	157
O3—H3A···Br1^{iii}	0.99	2.28	3.245 (4)	165
O3—H3B···O1^{iv}	0.83	2.18	2.961 (5)	157

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CS2117).

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supporting information

Acta Cryst. (2009). E**65**, m621 [doi:10.1107/S1600536809016316]

catena-Poly[hemi(hexane-1,6-diammonium) [[aquadibromidomanganese(II)]-μ-pyridine-2-carboxylato]]

Nam-Ho Kim, In-Chul Hwang and Kwang Ha

S1. Comment

Complex polymers are attracting great attention because of their potential applications such as in catalysis, magnetism, molecular recognition and other fileds (Huang *et al.*, 2004). The title compound, $\{(C_6H_{18}N_2)_{0.5}[MnBr_2(C_6H_4NO_2)(H_2O)]\}_n$, consists of an anionic complex chain polymer with counter-cations (Fig. 1). In the anionic polymer, symmetry related Mn^{2+} ions are bridged by pyridinecarboxylate (pic) anion ligands to form one-dimensional zigzag chain structures along the *c* axis (Fig. 2). The Mn ion is six-coordinated in a distorted octahedral structure by one N atom of the pyridine ring, two O atoms of two carboxylate groups, one O atom of the water molecule and two Br atoms. The three O atoms are disposed in the facial position. The asymmetric unit contains the repeat unit of the polymer, $[MnBr_2(C_6H_4NO_2)(H_2O)]^-$, and one half of a 1,6-diammoniohexane cation. Cations sit on a 2-fold symmetry axes at 0, *y*, 1/4 (Wyckoff letter *e*). The compound displays intermolecular hydrogen bonding (Table 1). There may be also intermolecular π-π interactions between adjacent pyridine rings, with a centroid-centroid distance of 3.992 (4) Å. The structure of the anionic complex polymer is very similar to the structure of the neutral compound $[MnCl(pic)(H_2O)_2]_n$ in which the Mn ions are linked to each other by pyridinecarboxylate bridges in a *syn* - *anti* mode (Huang *et al.*, 2004).

S2. Experimental

A solution of $MnBr_2.4H_2O$ (0.116 g, 0.404 mmol), pyridine-2-carboxylic acid (0.101 g, 0.734 mmol) and 1,6-diamino-hexane (0.021 g, 0.184 mmol) in H_2O (10 ml) was refluxed for 4 h. The solvent was removed under vacuum and the residue was dried at 70 °C, to give a pale yellow film. Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_3CN solution.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.93 Å (aromatic) or 0.97 Å (CH_2) and N—H = 0.89 Å, and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(N)]. The H atoms of the water molecule were located from Fourier difference maps, but not refined.

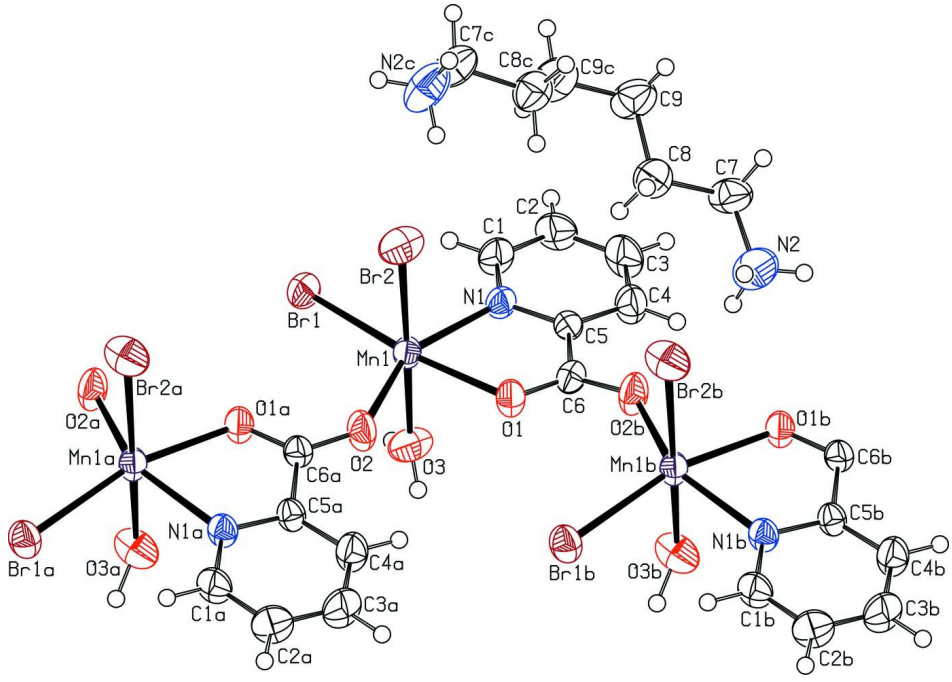

Figure 1

A structure detail of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms [Symmetry codes: (*a*) *x*, -*y*, -1/2 + *z*, (*b*) *x*, -*y*, 1/2 + *z*, (*c*) -*x*, *y*, 3/2 - *z*].

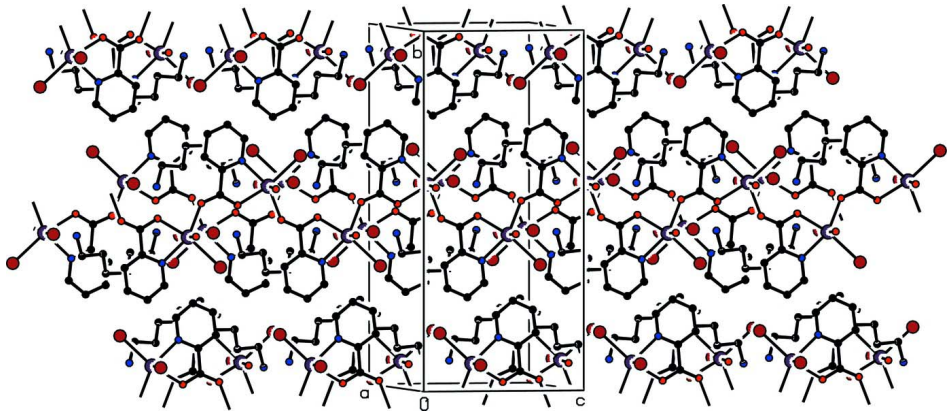

Figure 2

View of the unit-cell contents and chain structure of the title compound. H atoms have been omitted for clarity.

catena-Poly[hemi(hexane-1,6-diammonium) [[aquadibromidomanganese(II)]-μ-pyridine-2-carboxylato]]

Crystal data

$(C_6H_{18}N_2)_{0.5}[MnBr_2(C_6H_4NO_2)(H_2O)]$
M_r = 413.99
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 13.490 (3) Å
b = 21.510 (5) Å
c = 9.803 (2) Å
β = 91.125 (4)°
V = 2843.9 (11) Å^3
Z = 8
F(000) = 1616
D_x = 1.934 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 806 reflections
θ = 2.8–25.3°
μ = 6.55 mm^{-1}

T = 293 K
Stick, colorless

0.10 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.394, T_{max} = 0.520

7815 measured reflections
2705 independent reflections
1846 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.7°, θ_{min} = 1.8°
h = −16→15
k = −26→26
l = −7→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.114
S = 0.94
2705 reflections
152 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.32935 (6)	0.06982 (4)	0.41356 (8)	0.0340 (2)
Br1	0.34335 (4)	0.15379 (3)	0.21825 (6)	0.0438 (2)
Br2	0.13026 (5)	0.06928 (3)	0.40001 (8)	0.0585 (2)
O1	0.3336 (3)	0.01771 (15)	0.6076 (4)	0.0406 (10)
O2	0.3331 (3)	−0.02393 (17)	0.3343 (4)	0.0491 (11)
O3	0.4928 (3)	0.06506 (18)	0.4217 (5)	0.0549 (12)
H3A	0.5358	0.0983	0.3865	0.082*
H3B	0.5394	0.0408	0.4376	0.082*
N1	0.3431 (3)	0.14114 (19)	0.5834 (4)	0.0349 (11)
C1	0.3514 (4)	0.2031 (2)	0.5714 (6)	0.0442 (15)
H1	0.3488	0.2203	0.4844	0.053*
C2	0.3634 (5)	0.2422 (3)	0.6809 (7)	0.0519 (16)
H2	0.3667	0.2850	0.6687	0.062*
C3	0.3702 (5)	0.2168 (3)	0.8077 (7)	0.0558 (18)
H3	0.3800	0.2422	0.8836	0.067*
C4	0.3625 (5)	0.1532 (3)	0.8234 (6)	0.0470 (15)
H4	0.3667	0.1351	0.9095	0.056*
C5	0.3488 (4)	0.1175 (2)	0.7091 (5)	0.0318 (12)
C6	0.3378 (4)	0.0470 (3)	0.7180 (6)	0.0343 (13)
N2	0.1654 (3)	0.06720 (19)	1.0558 (5)	0.0717 (19)
H2A	0.2232	0.0622	1.0151	0.107*
H2B	0.1262	0.0350	1.0366	0.107*
H2C	0.1754	0.0696	1.1457	0.107*

C7	0.1177 (3)	0.12511 (19)	1.0062 (5)	0.0564 (18)
H7A	0.1654	0.1588	1.0122	0.068*
H7B	0.0630	0.1353	1.0650	0.068*
C8	0.0796 (5)	0.1202 (3)	0.8624 (7)	0.0545 (17)
H8A	0.0399	0.0828	0.8525	0.065*
H8B	0.1351	0.1169	0.8013	0.065*
C9	0.0174 (5)	0.1762 (3)	0.8230 (7)	0.065 (2)
H9A	−0.0400	0.1777	0.8810	0.078*
H9B	0.0560	0.2136	0.8400	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0451 (5)	0.0302 (4)	0.0267 (5)	0.0019 (4)	0.0001 (4)	0.0004 (4)
Br1	0.0526 (4)	0.0416 (3)	0.0371 (4)	0.0026 (3)	0.0016 (3)	0.0072 (3)
Br2	0.0466 (4)	0.0593 (4)	0.0697 (5)	0.0030 (3)	0.0012 (3)	0.0179 (4)
O1	0.068 (3)	0.0250 (19)	0.029 (2)	−0.0015 (18)	0.001 (2)	0.0003 (17)
O2	0.082 (3)	0.036 (2)	0.029 (2)	0.003 (2)	−0.001 (2)	−0.0072 (18)
O3	0.042 (2)	0.055 (3)	0.068 (3)	0.008 (2)	0.005 (2)	0.021 (2)
N1	0.045 (3)	0.029 (3)	0.031 (3)	0.002 (2)	0.000 (2)	0.004 (2)
C1	0.062 (4)	0.028 (3)	0.043 (4)	−0.002 (3)	0.001 (3)	0.009 (3)
C2	0.066 (4)	0.029 (3)	0.061 (4)	0.001 (3)	0.003 (4)	−0.005 (3)
C3	0.082 (5)	0.034 (3)	0.051 (4)	−0.004 (3)	0.001 (4)	−0.015 (3)
C4	0.069 (4)	0.037 (3)	0.035 (3)	0.001 (3)	0.000 (3)	−0.001 (3)
C5	0.038 (3)	0.029 (3)	0.028 (3)	0.004 (2)	0.004 (2)	0.001 (2)
C6	0.036 (3)	0.038 (3)	0.030 (3)	−0.002 (2)	−0.001 (3)	0.005 (3)
N2	0.092 (5)	0.050 (3)	0.072 (4)	0.012 (3)	−0.031 (4)	−0.015 (3)
C7	0.051 (4)	0.050 (4)	0.067 (5)	0.009 (3)	−0.016 (4)	−0.012 (4)
C8	0.050 (4)	0.060 (4)	0.053 (4)	0.001 (3)	−0.005 (3)	−0.003 (3)
C9	0.079 (5)	0.042 (4)	0.073 (5)	0.007 (4)	−0.019 (4)	−0.003 (4)

Geometric parameters (Å, º)

Mn1—O2	2.162 (4)	C4—C5	1.368 (7)
Mn1—O3	2.206 (4)	C4—H4	0.93
Mn1—O1	2.208 (4)	C5—C6	1.526 (7)
Mn1—N1	2.269 (4)	C6—O2^{ii}	1.247 (6)
Mn1—Br1	2.6416 (11)	N2—C7	1.4799
Mn1—Br2	2.6864 (12)	N2—H2A	0.89
O1—C6	1.253 (6)	N2—H2B	0.89
O2—C6^{i}	1.247 (6)	N2—H2C	0.89
O3—H3A	0.99	C7—C8	1.495 (7)
O3—H3B	0.83	C7—H7A	0.97
N1—C5	1.334 (6)	C7—H7B	0.97
N1—C1	1.343 (6)	C8—C9	1.514 (8)
C1—C2	1.371 (8)	C8—H8A	0.97
C1—H1	0.93	C8—H8B	0.97
C2—C3	1.359 (9)	C9—C9^{iii}	1.497 (13)

C2—H2	0.93	C9—H9A	0.97
C3—C4	1.382 (8)	C9—H9B	0.97
C3—H3	0.93		

O2—Mn1—O3	86.53 (16)	C5—C4—H4	120.9
O2—Mn1—O1	80.53 (14)	C3—C4—H4	120.9
O3—Mn1—O1	86.35 (15)	N1—C5—C4	123.2 (5)
O2—Mn1—N1	153.14 (15)	N1—C5—C6	115.3 (5)
O3—Mn1—N1	86.42 (16)	C4—C5—C6	121.5 (5)
O1—Mn1—N1	73.17 (14)	O2^{ii}—C6—O1	126.0 (5)
O2—Mn1—Br1	112.02 (11)	O2^{ii}—C6—C5	117.1 (5)
O3—Mn1—Br1	88.42 (11)	O1—C6—C5	117.0 (5)
O1—Mn1—Br1	166.09 (10)	C7—N2—H2A	109.5
N1—Mn1—Br1	93.65 (11)	C7—N2—H2B	109.5
O2—Mn1—Br2	90.48 (12)	H2A—N2—H2B	109.5
O3—Mn1—Br2	176.99 (12)	C7—N2—H2C	109.5
O1—Mn1—Br2	92.83 (11)	H2A—N2—H2C	109.5
N1—Mn1—Br2	96.13 (12)	H2B—N2—H2C	109.5
Br1—Mn1—Br2	93.02 (3)	N2—C7—C8	112.9 (3)
C6—O1—Mn1	119.3 (3)	N2—C7—H7A	109.0
C6^{i}—O2—Mn1	134.6 (4)	C8—C7—H7A	109.0
Mn1—O3—H3A	123.2	N2—C7—H7B	109.0
Mn1—O3—H3B	142.1	C8—C7—H7B	109.0
H3A—O3—H3B	94	H7A—C7—H7B	107.8
C5—N1—C1	117.2 (5)	C7—C8—C9	111.3 (5)
C5—N1—Mn1	115.0 (3)	C7—C8—H8A	109.4
C1—N1—Mn1	127.7 (4)	C9—C8—H8A	109.4
N1—C1—C2	123.3 (6)	C7—C8—H8B	109.4
N1—C1—H1	118.4	C9—C8—H8B	109.4
C2—C1—H1	118.4	H8A—C8—H8B	108.0
C3—C2—C1	118.4 (6)	C9^{iii}—C9—C8	113.9 (5)
C3—C2—H2	120.8	C9^{iii}—C9—H9A	108.8
C1—C2—H2	120.8	C8—C9—H9A	108.8
C2—C3—C4	119.7 (6)	C9^{iii}—C9—H9B	108.8
C2—C3—H3	120.2	C8—C9—H9B	108.8
C4—C3—H3	120.2	H9A—C9—H9B	107.7
C5—C4—C3	118.3 (6)		

O2—Mn1—O1—C6	176.8 (4)	C5—N1—C1—C2	−1.1 (9)
O3—Mn1—O1—C6	89.7 (4)	Mn1—N1—C1—C2	−177.3 (4)
N1—Mn1—O1—C6	2.3 (4)	N1—C1—C2—C3	2.0 (10)
Br1—Mn1—O1—C6	21.6 (8)	C1—C2—C3—C4	−1.6 (10)
Br2—Mn1—O1—C6	−93.2 (4)	C2—C3—C4—C5	0.4 (10)
O3—Mn1—O2—C6^{i}	−89.0 (6)	C1—N1—C5—C4	−0.2 (8)
O1—Mn1—O2—C6^{i}	−175.9 (6)	Mn1—N1—C5—C4	176.5 (4)
N1—Mn1—O2—C6^{i}	−164.0 (5)	C1—N1—C5—C6	179.3 (5)
Br1—Mn1—O2—C6^{i}	−2.1 (6)	Mn1—N1—C5—C6	−4.0 (6)
Br2—Mn1—O2—C6^{i}	91.3 (5)	C3—C4—C5—N1	0.5 (9)

O2—Mn1—N1—C5	−10.9 (6)	C3—C4—C5—C6	−178.9 (5)
O3—Mn1—N1—C5	−86.0 (4)	Mn1—O1—C6—O2^{ii}	174.2 (4)
O1—Mn1—N1—C5	1.3 (4)	Mn1—O1—C6—C5	−5.2 (6)
Br1—Mn1—N1—C5	−174.2 (4)	N1—C5—C6—O2^{ii}	−173.3 (5)
Br2—Mn1—N1—C5	92.4 (4)	C4—C5—C6—O2^{ii}	6.3 (8)
O2—Mn1—N1—C1	165.3 (4)	N1—C5—C6—O1	6.2 (7)
O3—Mn1—N1—C1	90.3 (5)	C4—C5—C6—O1	−174.3 (5)
O1—Mn1—N1—C1	177.5 (5)	N2—C7—C8—C9	171.0 (4)
Br1—Mn1—N1—C1	2.1 (5)	C7—C8—C9—C9^{iii}	176.1 (7)
Br2—Mn1—N1—C1	−91.4 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1^{ii}	0.89	2.44	2.949 (6)	117
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N2—H2*B*···Br2^{ii}	0.89	2.61	3.339 (4)	139
N2—H2*C*···Br2^{iv}	0.89	2.58	3.417 (5)	157
O3—H3*A*···Br1^{v}	0.99	2.28	3.245 (4)	165
O3—H3*B*···O1^{vi}	0.83	2.18	2.961 (5)	157

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